

CHEMICAL BONDING

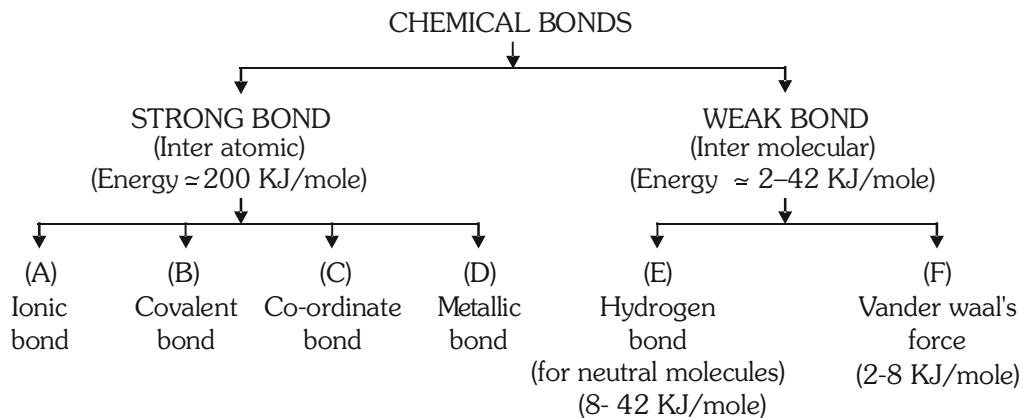
2.0 INTRODUCTION

- It is well known fact that except inert gases, no other element exists as independent atom under ordinary conditions.
- Most of the elements exist as molecules which are cluster of atoms. How do atoms combine to form molecules and why do atoms form bonds? Such doubts will be discussed in this chapter.
- A molecule will only be formed if it is more stable and has a lower energy, than the individual atoms.

Chemical Bond

- A force that acts between two or more atoms to hold them together as a stable molecule.
- It is union of two or more atoms involving redistribution of e^- among them.
- This process accompanied by decrease in energy.
- Decrease in potential energy (P.E.) \propto Strength of the bond.
- Therefore molecules are more stable than atoms.

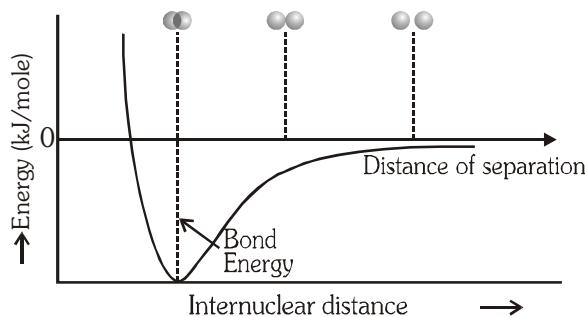
Classification of Bonds



Cause of Chemical Combination

(A) Tendency to acquire minimum energy

- When two atoms approaches to each other. Nucleus of one atom attracts the electron of another atom.
- Two nuclei and electrons of both the atoms repels each other.
- If net result is attraction, the total energy of the system (molecule) decreases and a chemical bond forms.
- So Attraction \propto 1/energy \propto Stability.
- Bond formation is an exothermic process



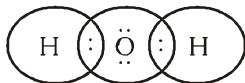
(B) Tendency to acquire noble gas configuration :

- Atom combines to acquire noble gas configuration.
- Only outermost electrons i.e. ns, np and (n-1)d shells electrons participate in bond formation.
- Inert gas elements do not participate in bond formation, as they have stable electronic configuration hence will have minimum energy. (Stable configuration $1s^2$ or ns^2np^6)

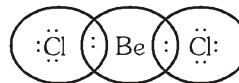


2.1 KOSSEL - LEWIS APPROACH TO CHEMICAL BONDING

- Every atom has a tendency to complete its octet in outermost shell
- H has the tendency to complete its duplet.
- To acquire inert gas configuration atoms loose or gain electron or share electron.
- The tendency of atoms to achieve eight electrons in their outer most shell is known as Lewis octet rule.



Obey octet rule



Doesn't obey octet rule

Exception of Octet Rule

(a) Incomplete octet molecules :- or (electron deficient molecules)

Compound in which octet is not complete in outer most orbit of central atom.

Example - Halides of IIIA groups, BF_3 , AlCl_3 , BCl_3 , hydride of III A/13th group etc.

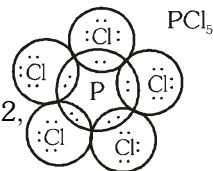


Other examples - BeCl_2 ($4e^-$), HgCl_2 ($4e^-$), $\text{Ga(CH}_3)_3$ ($6e^-$)

(b) Expansion of octet or (electron efficient molecules)

Compound in which central atom has more than $8e^-$ in outermost orbits.

Example - In PCl_5 , SF_6 and IF_7 , the central atom P, S and I contain 10, 12, and 14 electrons respectively.



(c) Pseudo inert gas configuration :-

Cations which contain 18 electrons in outermost orbit

Ex. Ga^{+3} , Cu^+ , Ag^+ , Zn^{+2} , Cd^{+2} , Sn^{+4} , Pb^{+4} etc.

Electronic configuration of Ga - $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^1$

Electronic configuration of Ga^{+3} - $1s^2, 2s^2, 2p^6, \underbrace{3s^2, 3p^6, 3d^{10}}_{18e^-}$

(d) Cations having electron between 9 to 17 in their outer most shell

Ex. Mn^{+2} , Fe^{+2} , Fe^{+3} , Ti^{+2} etc.

Electronic configuration of Fe - $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^2$

Electronic configuration of Fe^{+3} - $1s^2, 2s^2, 2p^6, \underbrace{3s^2, 3p^6, 3d^5}_{(\text{less than } 18e^-)}$

(e) Odd electron molecules :-

Central atom have an unpaired electron or odd no ($7e^-$, $11e^-$ etc) of electrons in their outer most shell.

e.g. NO , NO_2 , ClO_2 etc.



VALENCY

It is defined as the combining capacity of the elements. The word valency is derived from an Italian word "Valentia" which means combining capacity.

Old concept : Given by : **Frankland**

Valency with respect to Hydrogen : Valency of H = 1

It is defined as the number of hydrogen attached with a particular element.

	IA	IIA	IIIA	IVA	VA	VIA	VIIA
	NaH	MgH ₂	AlH ₃	SiH ₄	PH ₃	H ₂ S	HCl
Valency	1	2	3	4	3	2	1

Note : Valency w.r.t. H across the period increases upto 4 and then again decreases to 1.

Valency with respect to oxygen : Valency of 'O' = 2

It is defined as twice the number of oxygen atoms attached with a particular atom.

	IA	IIA	IIIA	IVA	VA	VIA	VIIA
	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl ₂ O ₇
Valency	1	2	3	4	5	6	7

Note : Valency with respect to oxygen increases from 1 to 7 across the period. Valency w.r.t. 'O' is equal to the group number.

New concept : This concept is based on the electronic configuration. According to this concept valency for IA to IVA group elements is equal to number of valence shell e^- and from VA to zero group, it is –

$$[8 - (\text{number of valence } e^-)]$$

$$\text{Valency} = \text{No. of valence } e^-$$

$$\text{Valency} = (8 - \text{no. of valence } e^-)$$

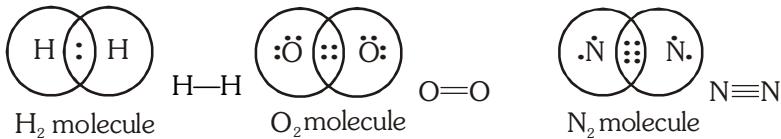
	IA	IIA	IIIA	IVA	VA	VIA	VIIA	0
	ns ¹	ns ²	ns ² np ¹	ns ² np ²	ns ² np ³	ns ² np ⁴	ns ² np ⁵	ns ² np ²
Valence	1	2	3	4	5	6	7	8
shell e^-								
Valency	1	2	3	4	3	2	1	0
					(8 - 5) = 3			(8 - 8) = 0

Note : All the elements of a group have same valencies because they have same number of valence shell electrons.



2.2 COVALENT BOND

- A covalent bond is formed by the mutual sharing of electrons between two atoms of electro negative elements to complete their octet. (Except H which completes its duplet)



- The shared pair of electrons should have opposite spins, and are localised between two atoms concerned.
- Sharing of electrons may occur in three ways –

No. of electrons shared between two atoms	Electron pair	Bond.
2	1	Single bond (—)
4	2	Double bond (==)
6	3	Triple bond (≡)

Examples – $\begin{array}{c} \text{H} & \text{N} & \text{H} \\ & \text{H} \end{array}$ { Three single bonds (not triple bond)}

N≡N Triple bond. (not three single bonds) O=O Double bond (Not two single bonds) H—O—H (Two single bonds.)

Orbital Concept of Covalent Bond

- One orbital can accommodate maximum 2 electrons with opposite spins like $1\downarrow$
- Half filled orbital or unpaired electron orbital share one electron from another atom, to complete its orbital.
- Tendency to complete orbital or to pair the electron is an essential condition of covalent bond. Completion of octet is not the essential condition of covalent bond.
- Covalency** : It is the number of covalent bonds which an atom makes in a molecule.
- If the outermost orbital has empty orbitals then covalent bonds are formed in excited state.

2.3 VARIABLE VALENCY IN COVALENT BONDS

- Variable valencies are shown by those elements which have empty orbitals in outermost shell.
- Lone pair electrons get excited in the subshell of the same shell to form the maximum number of unpaired electrons. Maximum covalency is shown in excited state.
- The energy required for excitation of electrons is called promotion energy.
- Promotion rule – Excitation of electrons in the same orbit.

Example –

(a) Nitrogen → Ground state

$1\downarrow$	1	1	1
2s	2p		

Covalency 3 (NCl₃)

For Nitrogen → Excited states are not possible due to absence of vacant orbital that's why (NCl₅) does not exist

(b) Phosphorus → Ground state

$1\downarrow$	1	1	1
3s	3p		

Covalency 3 (PCl₃)

Phosphorus → Excited state

1	1	1	1	1	1	1
3s	3p					

Covalency – 5 (PCl₅)



Note :

NCl_3 — exists

NCl_5 — doesn't exist (due to absence of d-orbitals in Nitrogen.) While PCl_3 and PCl_5 both exist because 3d orbitals are present in phosphorus.

OF_2 — exists, but OF_4 and OF_6 doesn't exist due to absence of d-orbitals. While SF_4 and SF_6 exist due to presence of d-orbital which are present in its valence shell.

- It can explain existence of molecules.

(c) Sulphur \rightarrow Ground state.

$1\downarrow$	$1\downarrow$	1	1	\square	\square	\square	\square	Covalency - 2 (SF_2)
3s	3p			3d				

Sulphur \rightarrow Excited state

1 st excited state	$1\downarrow$	1	1	1	1	\square	\square	\square	Covalency - 4 (SF_4)
	3s	3p			3d				

2 nd excited state	1	1	1	1	1	1	\square	\square	Covalency - 6 (SF_6)
	3s	3p			3d				

So variable covalency of S is 2, 4, & 6.

(d) Iodine has three lone pair of electrons

(Ground state)	$1\downarrow$	$1\downarrow$	$1\downarrow$	1	\square	\square	\square	\square
	5s	5p		5d				

So it shows three excited states – Maximum number of unpaired electrons = 7

Variable Valencies are 1, 3, 5 and 7

2.4 CHARACTERISTIC OF COVALENT COMPOUND**(a) Physical state :-** Covalent compounds are found in all the three states - Gas, Solid & Liquid.

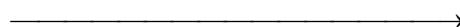
Separate molecules — In gaseous state

Associate molecules — In liquid & solid state

(Due to strong vander waal's force and hydrogen bonding among the molecules.)

As the molecular weight increases physical state changes -

eg.	F_2 and Cl_2	Br_2	I_2, At_2
	gas	liquid	solid



Top to bottom in a group. Vander waal's force increases between the molecules.

(b) Covalent solid :- Those solids in which atoms are linked together by covalent bonds, forms infinite three dimensional giant structure.

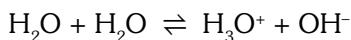
eg. Diamond, Graphite, AlN, SiC, SiO_2 etc.

Molecular solid :- Discrete (separate) molecules are formed by covalent bonds and then the molecules associates due to intermolecular force of attraction. (van der Waal force)

eg. Solid I_2 , dry ice (Solid CO_2) etc.



(c) Conductivity :- Mostly covalent compounds are bad conductor of electricity. But few polar covalent compounds due to self ionisation can conduct electricity. eg. H_2O , liq. NH_3 etc.



Free ions are formed which can conduct electricity.

Exceptions :- Graphite, HCl in water.

(d) Solubility :- Non polar compounds are soluble in non polar solvents. Non polar compounds forms vander waal bond with non polar solvent molecules.

Non polar solvents are C_6H_6 , CCl_4 etc.

(e) Isomerism :- Covalent bond is rigid and directional, so it shows isomerism.

eg. Organic compounds.

(f) Reaction :- Reaction between covalent compounds are slow. Because it involves breaking of old bonds and formation of new bonds.

BEGINNER'S BOX-1

1. Which condition favours the bond formation:

- (1) Maximum attraction and maximum potential energy
- (2) Minimum attraction and minimum potential energy
- (3) Minimum potential energy and maximum attraction
- (4) None of the above

2. Which one of the following element will never obey octet rule:

- (1) Na
- (2) F
- (3) S
- (4) H

3. Which is not an exception to octet rule ?

- (1) BF_3
- (2) SiCl_4
- (3) BeI_2
- (4) ClO_2

4. An oxide of chlorine which is an odd electron molecule is :

- (1) ClO_2
- (2) Cl_2O_6
- (3) Cl_2O_7
- (4) Cl_2O

2.5 VALENCE BOND THEORY (VBT) :

(A) It was presented by Heitler & London to explain how a covalent bond is formed.

It was extended by Pauling & Slater.

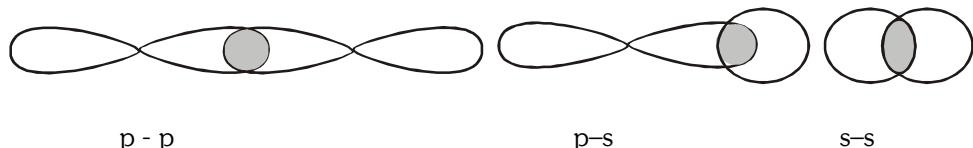
(B) The main points of theory are –

- (a) To form a covalent bond overlapping occurs between half filled valence shell orbitals of the two atoms.
- (b) Resulting bond acquires a pair of electrons with opposite spins to get stability.
- (c) Orbitals come closer to each other from the direction in which there is maximum overlapping
- (d) So covalent bond has directional character.
- (e) Strength of covalent bond \propto extent of overlapping.
- (f) Extent of overlapping depends on two factors.
 - (i) Nature of orbitals – p, d and f are directional orbitals \rightarrow more overlapping
 - s-orbital \rightarrow non directional – less overlapping



(ii) Nature of overlapping – Co-axial overlapping - extent of overlapping more.
Collateral overlapping - extent of overlapping less

Order of strength of Co - axial overlapping – $p - p > s - p > s - s$



(g) As the value of n increases, bond strength decreases.

$$1 - 1 > 1 - 2 > 2 - 2 > 2 - 3 > 3 - 3$$

$$1s - 2p > 2s - 2p > 3s - 3p$$

(h) If n is same $2p - 2p > 2s - 2p > 2s - 2s$

(i) Electron which is already paired in valency shell can enter into bond formation, if they can be unpaired first and shifted to vacant orbitals of slightly higher energy of the same energy shell.

(j) This point can explain the trivalency of boron, tetravalency of carbon, pentavalency of phosphorus etc.

(k) Two types of bonds are formed on account of overlapping.

Sigma (σ) Bond

(a) Bond formed between two atoms by the overlapping of half filled orbitals along their axis (end to end overlap) is called sigma bond.

(b) σ bond is directional.

(c) σ bond do not take part in resonance.

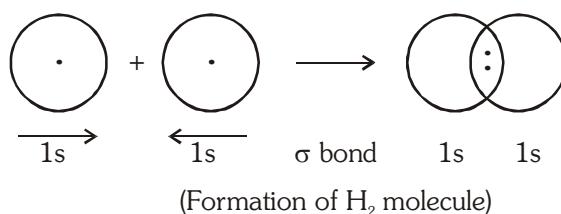
(d) Free rotation is possible about a single σ bond.

(e) Maximum overlapping is possible between electron clouds and hence it is strong bond.

(f) There can be only one σ bond between two atoms.

Sigma bonds are formed by four types of overlapping

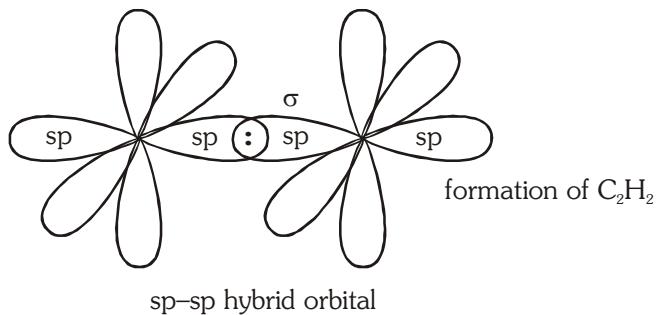
(i) s - s overlapping – Two half filled s-orbitals overlap along the internuclear axis. Ex. H_2 molecule.



(ii) s - p overlapping (Formation of HF) – When half fill s-orbital of one atom overlap with half filled p-orbital of other atom.

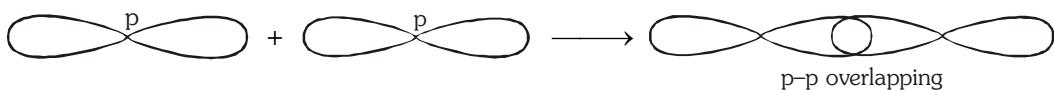


(iii) Bond between two hybrid orbitals – $sp^3 - sp^3$, $sp^2 - sp^2$, $sp^3 - sp^2$, $sp^3 - sp$ etc.



Note : overlapping of hybrid orbitals form σ bond.

(iv) p - p overlapping – (Coaxial) – It involves the coaxial overlapping between half filled p-orbitals of two different or same atoms.

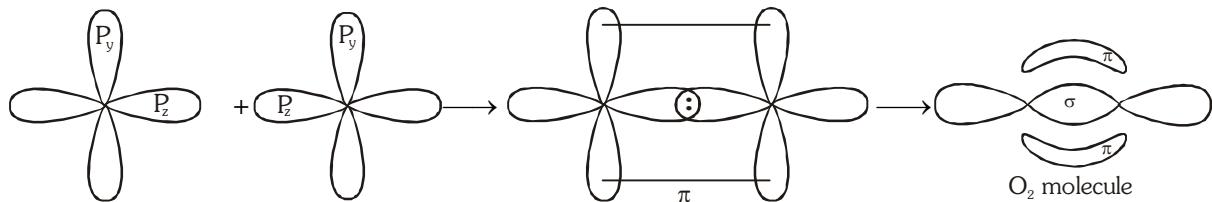


Ex. Formation of Cl_2 , F_2 , Br_2

Pi(π)-Bond

(a) The bond formed by sidewise (lateral) overlapping are known as π bonds.
 (b) Lateral overlapping is only partial, so formed are weaker and hence more reactive than σ bonds (Repulsion between nucleus is more as orbitals have to come much close to each other for π bonds formation)

Example – Formation of O_2 molecule –



Note : Only two p-orbitals of oxygen atom have unpaired e^- in each orbital for bonding.

Electron configuration of oxygen is – $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$

(c) Free rotation about a π bond is not possible.
 (d) π bond is weaker than σ bond (Bond energy difference is 63.5 KJ or 15 K cal/mole)
 (e) π bonds are less directional, so do not determine the shape of a molecule.
 (f) π bond takes part in resonance.
 (g) π bond formed by pure or unhybridized orbitals.

Comparison between σ and π bond

σ bond	π bond
<ol style="list-style-type: none"> Formed by axial overlapping Involves s-s, s-p, p-p (axial) & hybrid orbitals Extent of overlapping is more so stronger Free rotation around σ bond is possible Hybridized or unhybridized orbital forms σ bond Independent existence of σ-bond. 	<ol style="list-style-type: none"> Formed by side by side overlapping Involve p-p, p-d & d-d orbital Extent of overlapping is less so weaker Free rotation around π bond is not possible Hybridized orbital never forms π bond No independent existence.



BEGINNER'S BOX-2

Orbitals	Internuclear axis	Bond
s + s	any axis
s + px	x-axis
s + py	y-axis
s + pz	z-axis
px + px	x-axis
py + py	y-axis
pz + pz	z-axis
px + px	y or z-axis
py + py	x or z axis
pz + pz	x or y axis



2.6 HYBRIDISATION

Consider an example of Be compound :-

If it is formed without hybridisation then $\text{Cl} \text{---} \text{Be} \text{---} \text{Cl}$

both the Be-Cl bonds should have different parameters and p-p bond strength > s-p bond strength. But practically bond strength and distance of both the Be-Cl bonds are same.

This problem may overcome if hybridisation of s and p-orbital occurs.

Hybridisation

- (1) It is introduced by pauling, to explain equivalent nature of covalent bonds in a molecule.
- (2) **Definition** : Mixing of different shape and approximate equal energy atomic orbitals, and redistribution of energy to form new orbitals, of same shape & same energy. These new orbitals are called hybrid orbitals and the phenomenon is called hybridisation.

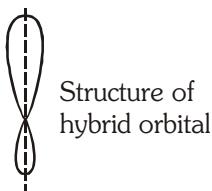
Now after considering s-p hybridisation in BeCl_2

$\text{Cl} \text{---} \text{sp} \text{---} \text{Be} \text{---} \text{p} \text{---} \text{Cl}$

(Bond strength of both the bonds will be equal)

Characteristic of Hybridisation

- (1) Hybridisation is a mixing of orbitals and not electrons. Therefore in hybridisation full filled, half filled and empty orbitals may take part.



- (2) Number of the hybrid orbitals formed is always be equivalent to number of atomic orbital which have taken part in the process of hybridisation.
- (3) Each hybrid orbital having two lobes, one is larger and other is smaller. Bond will be formed from large lobe.
- (4) The number of hybrid orbitals on central atom of a molecule or ion = number of σ bonds + lone pair of electron.
 - (i) The 1st bond between two atoms will be sigma.
 - (ii) The other bond between same two atoms will be pi bond.
 - (iii) The electron pair of an atom which do not take part in bond formation called as lone pair of electron.
- (5) One element can represent many hybridisation state depending on experimental conditions for example, C showing sp, sp^2 and sp^3 hybridisation in its compounds.
- (6) Hybrid orbitals are differentiated as sp, sp^2 , sp^3 etc.
- (7) The repulsion between $\text{lp} - \text{lp} > \text{lp} - \text{bp} > \text{bp} - \text{bp}$
- (8) The directional properties in hybrid orbital is more than atomic orbitals. Therefore hybrid orbitals form stronger sigma bond. The directional property of different hybrid orbitals will be in following order.
 $\text{sp} < \text{sp}^2 < \text{sp}^3 < \text{sp}^3\text{d} < \text{sp}^3\text{d}^2 < \text{sp}^3\text{d}^3$



DETERMINATION OF HYBRIDISATION STATE

Method (I) : Number of hybrid orbital = number of σ bond + number of lone pair [surrounding the central atom]

Method (II) : To predict hybridisation following formulae may be used :

$$\text{No. of hybrid orbital} = \frac{1}{2} [\text{Ve}^- + \text{SA} \pm \text{C}]$$

[Ve^- = Total number of valence e^- in the central atom, SA = total number of monovalent atoms; C = charge]

eg. NH_4^+ $\frac{1}{2} [5 + 4 - 1] = 4$ sp^3 hybridisation.

SF_4 $\frac{1}{2} [6 + 4] = 5$ sp^3d hybridisation.

SO_4^{2-} $\frac{1}{2} [6 + 2] = 4$ sp^3 hybridisation.

('O' is divalent so add only charge on anion)

NO_3^- $\frac{1}{2} [5 + 1] = 3$ sp^2 hybridisation.

If such type of e^- pairs are –

two	–	sp	hybridisation
three	–	sp^2	hybridisation
four	–	sp^3	hybridisation
five	–	sp^3d	hybridisation
six	–	sp^3d^2	hybridisation
seven	–	sp^3d^3	hybridisation

S.No.	Formula	Total pair of e^-		Hybridisation	Geometry	Ex.
		bp	lp			
1.	AB_2	2	0	sp	Linear	$\text{BeCl}_2, \text{CO}_2$
2.	AB_3	3	0	sp^2	Trigonal Planar	$\text{BCl}_3, \text{BF}_3$
3.	AB_4	4	0	sp^3	Tetrahedral	$\text{CH}_4, \text{CCl}_4$
4.	AB_5	5	0	sp^3d	Trigonal bipyramidal	PCl_5
5.	AB_6	6	0	sp^3d^2	Octahedral (Square bipyramidal)	SF_6
6.	AB_7	7	0	sp^3d^3	Pentagonal bipyramidal	IF_7

Position of lone pair & multiple bond

(i) $\text{sp}/\text{sp}^2/\text{sp}^3$ = Any where

(ii) sp^3d = equatorial

(iii) sp^3d^2 = axial (defined first)

(iv) sp^3d^3  Lone pair = 1 then equatorial
Lone pair = 2 then axial

(v) sp^3d hybridisation Axial bond length > equatorial bond length
 sp^3d^3 hybridisation Axial bond length < equatorial bond length

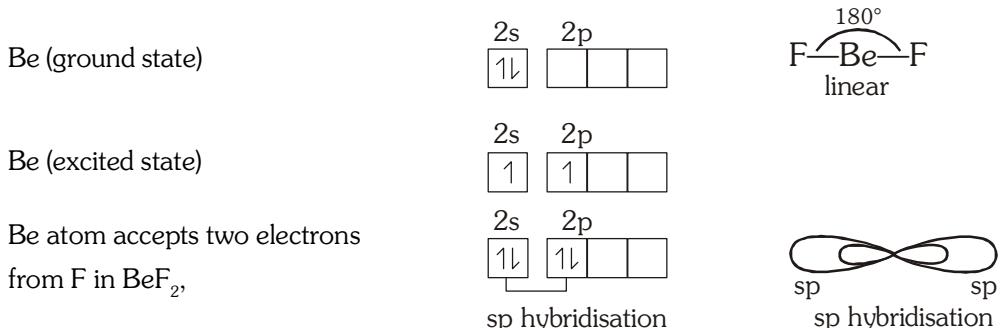
terminal atom same



Types of Hybridisation

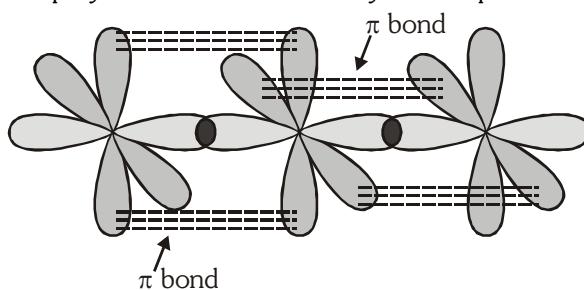
(A) sp hybridisation :

- (a) In this hybridisation one s- & one p- orbital of an atom are mixed to give two new hybrid orbitals which are equivalent in shape & energy known as sp hybrid orbitals.
- (b) These two sp hybrid orbitals are arranged in straight line & at bond angle 180° .
- (c) s-character 50%



CO_2 Molecule ($\text{O} = \text{C} = \text{O}$) :

In CO_2 molecule, C has two sp hybrid orbitals & two unhybridised p orbitals.



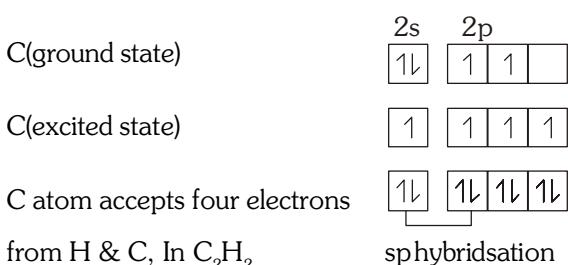
Molecular orbital picture of CO_2

Thus, CO_2 molecule is a linear in shape & having 180° bond angle.

The bond length between C–O bond is reduced due to the presence of π bond.



In $\text{CH} \equiv \text{CH}$ molecules, each C atom contains two sp hybrid orbitals & two unhybridised p orbitals



- sp hybrid orbital of each C overlaps to give sigma bond between C – C.
- The remaining one sp hybrid orbital of each C atom overlaps with s orbital of H, forming sigma bond between C – H.
- The two unhybridised p orbitals of each C atom (p_y and p_x) overlap laterally to form two pi(π) bonds.
- Therefore in $\text{H}-\text{C}_A \equiv \text{C}_B-\text{H}$
 - sigma bond between $\text{C}_A - \text{C}_B$ is formed sp – sp overlapping
 - sigma bond between $\text{C}_A - \text{H}$ is formed sp – s overlapping
 - sigma bond between $\text{C}_B - \text{H}$ is formed sp – s overlapping
 - pi bond between $\text{C}_A - \text{C}_B$ is formed : $p_y - p_y$, $p_x - p_x$ overlapping
- Each C atom forms two sigma bonds but in C_2H_2 , total sigma bonds are 3
- Each C atom forms two π bonds. Total π bonds in C_2H_2 are two
- Total number of bonds in acetylene are : $3\sigma + 2\pi$ bond = 5 bonds.



(B) **sp² Hybridisation :**

- (a) In this hybridisation one s & two p orbitals are mixed to give three new sp² hybrid orbitals which are in same shape & equivalent energies.
- (b) These three sp² hybrid orbitals are at angle of 120° & giving trigonal planar shape.

B (ground state)

2s	2p
1l	1 1 1

B (excited state)

1	1 1	1	1
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B atom accepts 3 electrons

1l	1l	1l	1
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From 3 F atoms in BF₃

sp² hybrid orbitals

- (c) s - character 33.3 %

- SnX₂ having two σ bonds & one l.p. electron therefore hybridisation is sp²
- The bond angle in SnX₂ will be less than 120° (due to presence of one l.p.e⁻).
- The shape of SnX₂ molecule is bent.

(C) **sp³ Hybridisation :**

- (I) In this hybridisation one s orbital and three p orbitals of an atom of a molecule or ion, are mixed to give four new hybrid orbitals called as sp³ hybrid orbitals.
- (II) The angle between hybrid orbitals will be 109° 28' (6)

C (ground state)

2s	2p
1l	1 1

C (excited state)

1	1	1	1
---	---	---	---

C atom in CH₄

1l	1l	1l	1l
----	----	----	----

sp³hybridisaion

C atom share four electrons with four hydrogen atoms

- (III) The shape obtained from these hybrid orbitals would be tetrahedron.

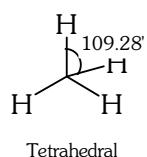
Three following examples represent this condition.

(a) **Four sigma bonds with zero lone pair electron :**

- (I) The following examples represent this condition.

CH₄, CF₄, CCl₄, CBr₄, Cl₄, NH₄⁺, BF₄⁻, BeF₄⁻²

- (II) In above compounds, bond angle is 109° 28' & tetrahedron shape.



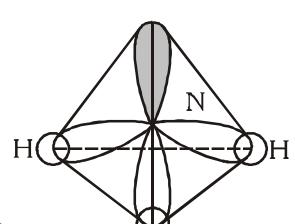
(b) **Three sigma bonds & one lone pair of electron :**

- (I) This condition is shown by following compounds & ions.

NH₃, NF₃, PF₃, NCl₃, PCl₃, :CH₃⁻, H₃O⁺, ClO₃⁻

- (II) sp³ hybridisation, pyramidal shape & bond angle will be less than 109° 28'.

Due to the presence of one lone pair electron on nitrogen it repels bond pair electron more therefore bond angle reduced from 109° 28' to 107°. The repulsion between lp - bp > bp - bp.



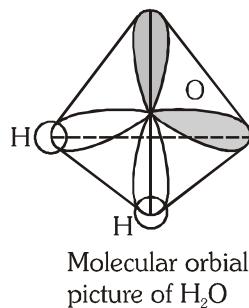
(c) Two sigma bonds & two lone pair of electrons :

(I) This condition is shown by following compounds and ions.

H_2O , OCl_2 , OBr_2 , OF_2 , OI_2 etc.

(II) In all above examples, the central atom showing sp^3 hybridisation, angular shape and bond angle will be either less than $109^\circ 28'$ or more than $109^\circ 28'$.

In H_2O the hybridisation on O atom is sp^3 , but due to presence of two lone pair electrons they repel each other

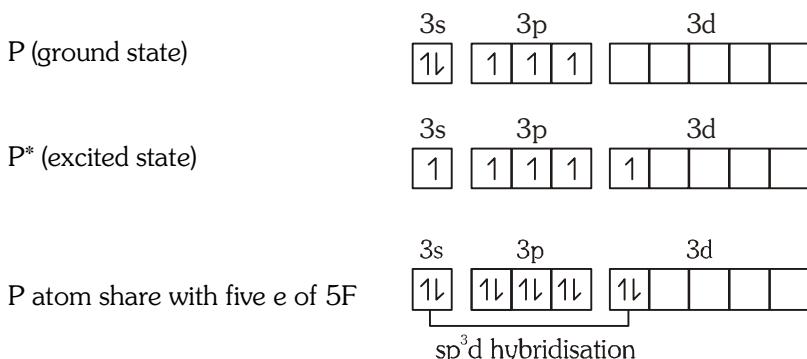


(D) sp^3d Hybridisation :

(I) In this hybridisation one s orbital, three p orbitals and one d orbital are mixed to give five new hybrid orbitals which are equivalent in shape and energy called as sp^3d hybrid orbitals.

(II) Out of these five hybrid orbitals, three hybrid orbitals are at 120° angle and two hybrid orbitals are perpendicular to the plane of three hybrid orbitals that is trigonal planar, the shape of molecule becomes trigonal bipyramidal.

For example, PF_5 showing sp^3d hybridisation



(III) In this hybridisation d_{z^2} orbital is hybridised with s and p orbitals.

In this way five sp^3d hybrid orbitals form five sigma bond with five F atoms and give a molecule of PF_5 , shape of this molecule is trigonal bipyramidal.

Two axial P-Cl bonds are longer than three equatorial P-Cl bonds due to repulsion between 3 equatorial bp of e^- and 2 axial b.p. of e^-

In above hybridisation, there are four conditions.

(a) Five sigma bonds and zero lone pair electron :

The following examples represent this conditions.

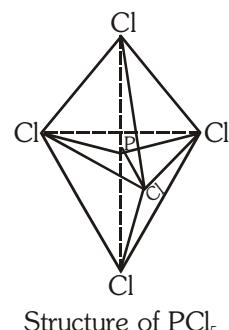
PCl_5 , PBr_5 , AsF_5 , AsCl_5 , SbCl_5 , SbF_5 etc.

The shape of all the above molecules is trigonal bipyramidal.

(b) Four sigma bonds and one lone pair of electron :

The following examples represent this condition.

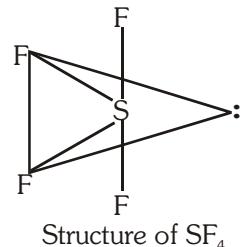
SF_4 , SeF_4 , TeF_4 , PoF_4 , PF_4^- , SbF_4^- , SCl_4 , SeCl_4 , TeCl_4 etc.



The shape of all above examples will be irregular tetrahedron or See-saw

Example SF_4

S ground state	3s	3p	3d
	1l	1l 1 1	
S excited state	3s	3p	3d
	1l	1 1 1	1
S atom share with four e^- from 4F atoms	3s	3p	3d
	1l	1l 1l 1l	1l
	five-sp ³ d orbitals		

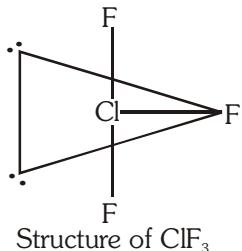


(c) Three sigma bonds & two lone pair of electrons :

The following examples represent this condition.

ClF_3 , BrF_3 , IF_3 , BrCl_3 , ICl_3 etc.

The shape of all above compounds is 'T' shape.



(d) Two sigma bonds & three lone pair of electrons :

The following examples represent this condition.

ICl_2^- , IBr_2^- , ClF_2^- , IF_2^- , BrF_2^- , XeF_2^- , I_3^- , Br_3^-

The geometry of above examples will be linear shape.

(E) sp^3d^2 Hybridisation :

- In this hybridisation, one s-orbital, three p-orbitals & two d-orbitals (dz^2 , dx^2-y^2) are mixed to give six new hybrid orbitals known as sp^3d^2 hybrid orbitals.
- The geometry of molecule obtained from above six hybrid orbitals will be symmetrical octahedral or square bipyramidal.
- The angle between all hybrid orbitals will be 90° .

Example : SF_6 , AlF_6^{-3} , PF_6^- , ICl_5 , XeF_4 , XeOF_4 , ICl_4^- ,

- Two 'd' orbital participates in the hybridisation are $\text{d}_{x^2-y^2}$ and d_{z^2} .

SF_6 S (ground state)

3s	3p	3d
1l	1l 1 1	

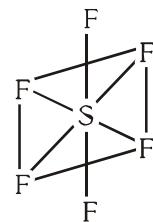
S (excited state)

3s	3p	3d
1	1 1 1	1 1

S (after hybridisation)

3s	3p	3d
1l	1l 1l 1l	1l 1l

sp^3d^2 hybridisation

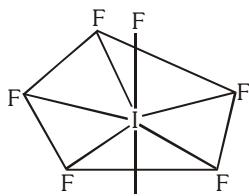


Octahedral or square bipyramidal.



(F) sp^3d^3 Hybridisation :

- (I) In this hybridisation, one s-orbital, three p-orbitals & three d-orbitals are mixed to give seven new hybrid orbitals known as sp^3d^3 hybrid orbitals.
- (II) These seven sp^3d^3 orbitals are configurated in pentagonal bipyramidal shape.
- (III) Five bond angles are of 72° and 10 bond angles of 90° .
- (IV) The following examples showing sp^3d^3 hybridisation - IF_7 & XeF_6 .



(Pentagonal bipyramidal)

EXAMPLES ON sp^3d HYBRIDISATION

Example	σ bond	l.p.e.	Hybridisation	Bond angle	Shape
PCl_5	5	-	sp^3d	$120^\circ, 180^\circ \& 90^\circ$	Trigonal bipyramidal
SF_4	4	1	sp^3d	$< 180^\circ, < 90^\circ, < 120^\circ$	Irregular tetrahedron
ClF_3	3	2	sp^3d	87.6°	T-shape
IF_3	3	2	sp^3d	87.6°	T-shape
ICl_3	3	2	sp^3d	87.6°	T-shape
Br_3^-	2	3	sp^3d	180°	Linear
ICl_2^-	2	3	sp^3d	180°	Linear
XeF_2	2	3	sp^3d	180°	Linear
PCl_4^+	4	-	sp^3		Tetrahedron
NH_4^+	4	-	sp^3		Tetrahedron
NF_3	3	1	sp^3		Pyramidal
H_3O^+	3	1	sp^3		Pyramidal
SO_3^{2-}	3	1	sp^3		Pyramidal
XeO_3	3	1	sp^3		Pyramidal
H_2O	2	2	sp^3		Angular (V)
NH_2^-	2	2	sp^3		Angular (V)
OF_2	2	2	sp^3		Angular (V)
Cl_2O	2	2	sp^3		Angular (V)
Diamond	4	-	sp^3		Tetrahedron
SiO_2	4	-	sp^3		Tetrahedron
SiC	4	-	sp^3		Tetrahedron
NO_3^-	3	-	sp^2	120°	Trigonal planar
SO_2	2	1	sp^2	$<120^\circ$	Angular (V)
HCO_3^-	3	-	sp^2	120°	Trigonal planar
$SnCl_2$	2	1	sp^2	$<120^\circ$	Angular (V)
NO_2^+	2	-	sp	180°	Linear
N_3^-	2	-	sp	180°	Linear



BEGINNER'S BOX-3

1. Which of the following is incorrect about hybridization?
 - (1) The concept of hybridization is not applied to isolated atoms.
 - (2) Hybridization is the mixing of at least two non-equivalent atomic orbitals.
 - (3) The number of hybrid orbitals generated is more than the number of pure atomic orbitals that participate in the hybridization process.
 - (4) Hybridization requires an input of energy.
2. The hybridization state of the central atom in HgCl_2 is-

(1) sp	(2) sp^2	(3) sp^3	(4) dsp^2
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3. The hybridization state of the central atom in AlI_3 is-

(1) dsp^2	(2) sp^3	(3) sp^2	(4) sp
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4. In C_3O_2 , the hybridization state of C is-

(1) sp^2	(2) sp	(3) sp^3	(4) dsp^2
------------	----------	------------	-------------
5. By hybridization, we mean the hybridization of-

(1) electrons	(2) atomic orbitals	(3) atoms	(4) protons
---------------	---------------------	-----------	-------------
6. The d- orbitals involved in sp^3d hybridisation is:-

(1) $d_{x^2-y^2}$	(2) d_{z^2}	(3) d_{xy}	(4) d_{xz}
-------------------	---------------	--------------	--------------
7. A sp^3 hybrid orbital contains:-

(1) $\frac{3}{4}$ s- character	(2) $\frac{1}{4}$ p - character	(3) $\frac{3}{4}$ p - character	(4) $\frac{1}{2}$ s - character
--------------------------------	---------------------------------	---------------------------------	---------------------------------
8. In the protonation of NH_3 molecule, following statement is true:-

(1) A covalent bond is formed	(2) Hydrogen bond is formed
(3) Hybridisation state of N is changed	(4) Shape of NH_3 molecule is changed
9. The shape of sulphate ion is :-

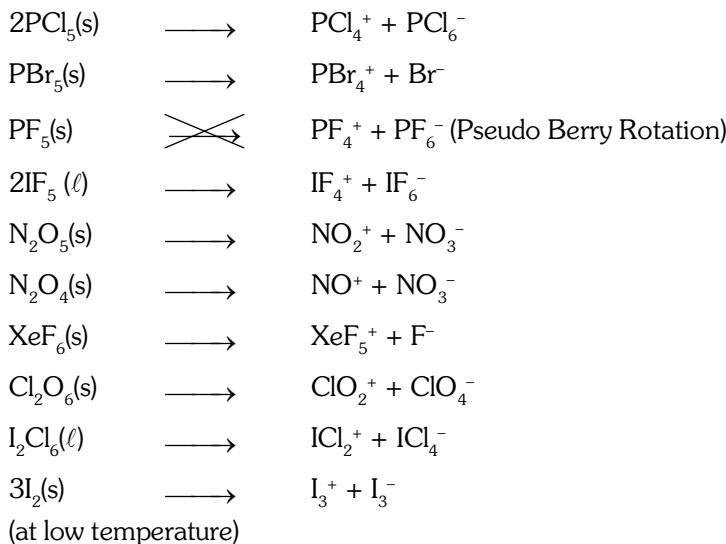
(1) Hexagonal	(2) Square planar
(3) Trigonal bipyramidal	(4) Tetrahedral
10. In which following compound, central atom has four bond pair and one lone pair:-

(1) NH_4^+	(2) ICl_4^-	(3) SF_4	(4) XeF_4
---------------------	----------------------	-------------------	--------------------
11. In which molecule s - p overlapping occurs ?

(1) CH_4	(2) NH_3	(3) H_2O	(4) None of these
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Hybridisation in solid state :

- Compounds which change their structure in solid state/liquid state.



Hybridisation in radicals :

Radical	hybridisation
CH ₃
CF ₃
ClO ₃
NO ₂

Existence and Nonexistence :

Identify existing / non existing compounds / ions

(a) PCl₆⁻ (b) NH₅ (c) PH₅ (d) (CCl₆)²⁻ (e) (SiF₆)²⁻ (f) (SiCl₆)²⁻ (g) ClBr₇
 (h) SH₆ (i) XeH₄ (j) XeOF₄ (k) FCl₃ (l) ClF₃ (m) BH₄⁻ (n) (PI₆)⁻

2.7 VALENCE SHELL ELECTRON PAIR REPULSION THEORY (VSEPR)

(a) If the central atom possess only bonded pairs of electrons along with identical atoms then shape of the compound is symmetrical and according to Sidgwick & Powl.

eg.	BF ₃	—	120°	—	triangular
	CH ₄	—	109° 28'	—	tetrahedral
	CO ₂	—	180°	—	linear

(b) If the central atom possess bonded pair of electrons as well as lone pair of electron, then shape of the molecule will be unsymmetrical ie. the original bond angle will disturbed due to repulsion between lone pair of electrons.

Similarly on having different type of side atoms, molecule becomes unsymmetrical due to unequal force of repulsion between e⁻. Order of repulsion is - [lp - lp > lp - bp > bp - bp]

$$\left[\text{Bond angle} \propto \frac{1}{\text{Number of lone pair of electrons}} \right]$$

(c) By increasing one lone pair of electron, bond angle is decreased approx by 2.5°.

eg.:-	CH ₄	NH ₃	H ₂ O	→	sp ³
	109°	107°	105°		hybridisation

2.8 BOND PARAMETERS

Bond Length

The average distance between the nucleus of two atoms is known as bond length, normally it is represented in Å. eg. A — B

It depends mainly on electronegativities of constituent atoms.

Case - I. Electronegativity difference is zero then -

$$\text{Bond length} = r_A + r_B \quad \text{or} \quad d_{A-B} = r_A + r_B$$

where r_A = covalent radius of A

r_B = covalent radius of B

x_A = electronegativity of A

x_B = electronegativity of B

If $r_A = r_B$ then Bond length = $2r_A$ or $2r_B$

Example : - Cl - Cl

Case - II Electronegativity difference is not equal to zero then -

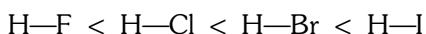
Bond length is given by Shomaker & Stevenson formula is - Bond length = $r_A + r_B - 0.09 (x_A - x_B) \text{ \AA}$

$(x_A - x_B)$ = Difference in electronegativities



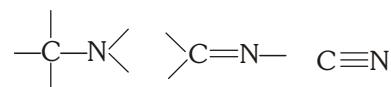
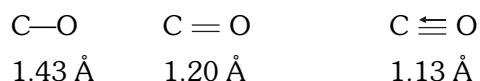
Factors Affecting Bond Length

(a) **Δ electronegativity** :- Bond length $\propto \frac{1}{\Delta EN}$ {While B.E. $\propto \Delta EN$ }



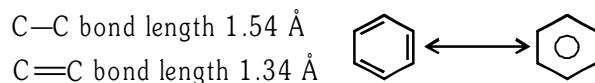
(b) **Bond order or number of bonds** :- Bond length $\propto \frac{1}{\text{Number of bonds or bond order}}$

Bond energy \propto Number of bond



(c) **Resonance** :- Due to resonance bond length affected

Ex.1. Benzene



But bond length is between single and double bond is = 1.39 Å

Ex.2. Bond length of C—O in CO_2 is 1.15 Å Resonance occurs in CO_2 is as follows -

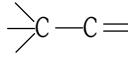
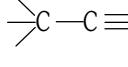


Bond length = 1.15 Å (Between double & triple bond)

(d) **Hybridization** :- Bond length $\propto \frac{1}{s \text{ character}}$

Example :-

s-character increases

Compound	Hybridisation	Bond length
Ethane	$sp^3—sp^3$	1.54 Å
	$sp^3—sp^2$	1.51 Å
	$sp^3—sp$	1.47 Å
$C=C-C=C$	$sp^2—sp^2$	1.46 Å
$C=C-C\equiv C$	$sp^2—sp$	1.42 Å
$C\equiv C-C\equiv C$	$sp—sp$	1.37 Å

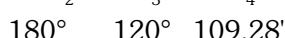
Bond Angle

The minimum angle between any two adjacent bonds is known as bond angle.

It is represented in degree (°), min (') and second (")

Factors affecting the bond angle -

Step I : Hybridisation or % 's' character : Bond angle \propto % s character



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9810934436, 8076575278, 8700391727

Step II : Lone pair

When hybridisation is same, lone pair are different.

$$\boxed{\text{Bond angle} \propto \frac{1}{\text{No. of lone pair}}}$$

Example :-

	CH_4	NH_3	$\text{H}_2\ddot{\text{O}}$:
Hybridisation	sp^3	sp^3	sp^3
Bond angle	109	> 107	> 105

No l.p. one l.p. two l.p.

- In the different molecules if central atom have same number of lone pair of electron then bond angle will depend on electronegativities of A & B.

Step III : Central Atom

$$\boxed{\text{Bond angle} \propto \text{Electronegativity of central atom}}$$

In AB_x type of molecules if side atoms are same and EN of central atom increases the bond angle increases.



- Electronegativity of 'O' > Electronegativity of 'S'
- Bond angle of $-\text{NH}_3 > \text{PH}_3 > \text{AsH}_3$

Example :-

	NH_3	PH_3	AsH_3
Bond angle	107°	93°	91°

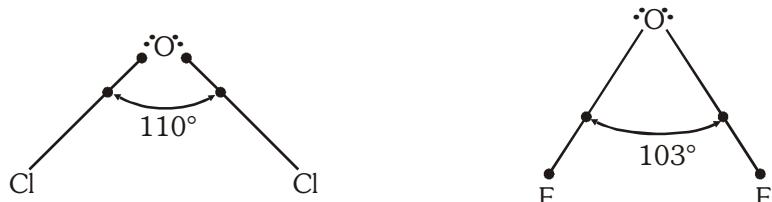
→

- Electronegativity decreasing.
- Bond angle will decrease

Step IV : Side atom

$$\boxed{\text{Bond angle} \propto \frac{1}{\text{electronegativity}} \propto \text{size of side atom of bonded atom}}$$

In AB_x type molecules, if central atoms are same and the EN of side atoms increases then bond angle decreases.



Electronegativity of Fluorine is greater than chlorine

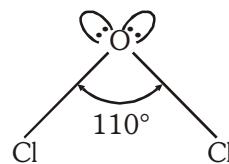
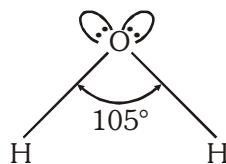
$\text{PF}_3 < \text{PCl}_3 < \text{PBr}_3 < \text{PI}_3$ (EN of side atom decrease)

$\text{OF}_2 < \text{Cl}_2\text{O} < \text{Br}_2\text{O}$

$\text{SF}_2 < \text{SCl}_2 < \text{SBr}_2$



Bond angle depends on size of side atom, On increasing size of side atom bond angle increases.



When hybridisation is same, lone pair are same, Central atom is same, bonded atoms are different.

sp ³	OF ₂	103 - 105°	Electronegativity of bonded atom is decreasing
sp ³	Cl ₂ O	109 - 111°	
sp ³	Br ₂ O	116 - 118°	

Bond Energy (BE)

Bond energy may be defined as -

- Bond formation energy :- Energy released when any bond is formed is known as bond formation energy or bond energy.
- Bond dissociation energy :- Energy required to dissociate any bond is known as Bond dissociation energy. Calculation of released energy is more difficult than the dissociation energy therefore dissociation energy of bond is calculated and is assumed as bond energy or bond formation energy.

Case-I In diatomic molecule :

$$\text{Bond energy} = \text{bond dissociation energy}$$

$$\text{Example: } \text{N}_2 > \text{O}_2 > \text{H}_2 > \text{F}_2$$

Case-II For polyatomic molecule :-

$$\text{Bond energy} \approx \text{Bond dissociation energy (D)}$$

Factors Affecting The Bond Energy

(a) Δ Electronegativity	(b) Bond order	(c) Atomic size	(d) Bond polarity
(e) Resonance	(f) Hybridisation	(g) Lone pair electron	

(a) Δ Electronegativity :- Bond energy $\propto \Delta\text{EN}$ eg. HF > HCl > HBr > HI

(b) Bond order :- Bond energy \propto Bond order.

$$\text{eg. } \text{C—C} < \text{C=C} < \text{C}\equiv\text{C} \\ 79 \text{ K. Cal.} \quad 143.3 \text{ K. Cal.}, \quad 199.0 \text{ K. Cal.}$$

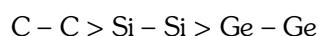
(c) Atomic size :- Bond energy $\propto \frac{1}{\text{Atomic size}}$ eg. C≡C < C≡N < N≡N

Exception :- In case of halogen group, order of bond energy is –



Because of higher electron density and small size of F atoms, repulsion between electrons of two F atoms, weakens the bond energy.

Other examples – S > O – O



(d) Bond Polarity :- Bond energy \propto Bond polarity



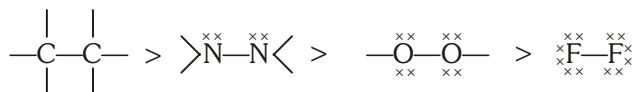
(e) Resonance :- Bond energy increases due to resonance.

eg. In benzene bond energy of C—C increases due to π electrons of C = C.

(f) Hybridisation :- Bond energy \propto s-character in hybrid orbitals.

eg. $sp-sp > sp^2-sp^2 > sp^3-sp^3$
s.character - 50 % 33.3 % 25 %

(g) Lone pair of electrons :- Bond energy $\propto \frac{1}{\text{lone pair of electrons}}$



Size of F and O atoms are small so their bond energy should be high (small atomic radius) but it is actually less, due to lone pair of electrons present on F and O atoms, which repels each other in F—F and —O—O-type of bonds.

Important Note (Summary) :

(i) Bond strength \propto overlapping (if orbitals are given)

(ii) Bond strength $\propto \frac{1}{\text{size of orbitals}}$

e.g. $1s - 2p > 1s - 3p > 1s - 4p$

(iii) If orbitals are of same shell

Bond strength \propto extent of overlapping \propto directional properties

$2p - 2p > 2s - 2p > 2s - 2s > 2p - 2p$ (Side ways)
 $\underbrace{}_{\text{Axial overlap}}$

(iv) π -bond strength

$2p\pi - 2p\pi > 2p\pi - 3d\pi > 2p\pi - 3p\pi > 3p\pi - 3p\pi$

(v) O = O exist but S = S does not exist at room temperature.

(vi) N ≡ N exist but P≡P does not exist at room temperature.

(vii) O=C=O exist but O=Si=O does not exist.

BEGINNER'S BOX-4

- Which of the following molecules has the longest nitrogen-nitrogen bond?
(1) N_2H_4 (2) N_2
(3) N_2F_2 (4) All have equal bond lengths
- Which of the following molecules has the highest value of carbon-carbon bond energy ?
(1) C_2H_4 (2) C_3H_8 (3) C_2H_2 (4) C_2H_6
- Which of the following has the shortest bond length ?
(1) Br_2 (2) F_2 (3) Cl_2 (4) I_2
- In ethene, the carbon-carbon bond distance is—
(1) 154 pm (2) 120 pm (3) 134 pm (4) 142 pm
- Carbon-halogen bond is strongest in the following
(1) CH_3Cl (2) CH_3Br (3) CH_3F (4) CH_3I
- The correct order of bond length is
(1) C — C < C = C < C ≡ C (2) C ≡ C < C = C < C — C
(3) C = C < C ≡ C < C — C (4) C = C < C — C < C ≡ C
- The F-F bond is weak because :
(1) The repulsion between the nonbonding pairs of electrons of two fluorine atoms is large
(2) The ionization energy of the fluorine atom is very low
(3) The length of the F-F bond much larger than the bond lengths in other halogen molecules
(4) The F-F bond distance is small and hence the internuclear repulsion between the two F atoms is very low
- The correct order of decreasing bond energy is:-
(1) O—O > S — S > Se — Se (2) C — C > Si — Si > Ge — Ge
(3) F — F > O — O > N — N (4) F — F > Cl — Cl > Br — Br



9. The bond length does not affect by:-
 (1) Electron affinity (2) Bond order (3) Hybridisation (4) Resonance

10. In allene structure three carbon atoms are joined by :
 (1) Three sigma bonds and three pi bonds (2) Two sigma bonds and one pi bond
 (3) Two sigma bonds and two pi bonds (4) Three pi bonds only

2.9 DIPOLE MOMENT

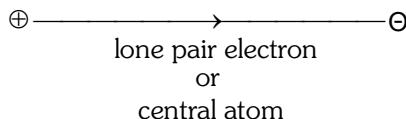
POLARITY OF BOND (IONIC NATURE IN COVALENT BOND)

(a) Polarity of any polar covalent bond or molecule is measured in terms of dipole moment.

(b) For measurement of extent of polarity, Pauling introduced the concept of dipole moment (μ).
 The product of positive or negative charge (q) and the distance (d) between two poles is called dipole moment.
 Here - $\vec{\mu} = q \times d$ (magnitude of charge \times distance),

(c) Dipole moment is a vector quantity i.e. it has both magnitude as well as direction.

(d) Direction of dipole moment is represented by an arrow pointing from electro +ve to electro -ve element and from central atom to lone pair of electrons.



(e) Unit of dipole moment is Debye
 $1 \text{ Debye} = 1 \times 10^{-18} \text{ e.s.u. cm} = 3.33 \times 10^{-30} \text{ coulomb metre}$

(f) In the diatomic molecule μ depends upon difference of EN i.e. $\mu \propto \Delta \text{EN}$
 order of μ , H-F > H-Cl > H-Br > H-I
 $\mu = 0$ for H-H, F-F, Cl-Cl, Br-Br, O-O

(g) For polyatomic molecules μ depends on the vector sum of dipole moments of all the covalent bonds.

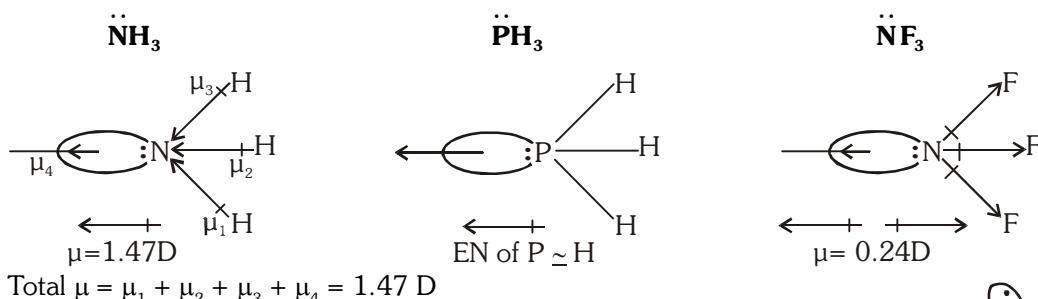
(h) For PCl_5 and SF_6 , etc. $\mu = 0$ due to their symmetrical geometry (According to charge).

(i) Benzene, naphthalene, diphenyl have $\mu = 0$ due to planar structure.

(j) If the vector sum is zero, then compound is non-polar compound or symmetrical compound (and it is not essential that individual μ of every bond should be zero).

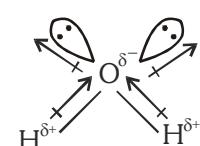
Example - BX_3 , CCl_4 , SiCl_4 , CH_4 , CO_2 , CS_2 , PCl_5 , SiH_4 etc.

In these examples the bond B-F, C-Cl, C-H, C-O, P-Cl etc. are polar even though compounds are non-polar.

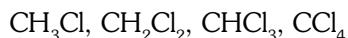


(k) Dipole moment of H_2O is 1.85 D which is resultant μ of two O-H bonds.
 μ of $\text{H}_2\text{O} > \mu$ of H_2S because electronegativity of oxygen is higher than sulphur.

(l) Angular structure of molecule have greater dipole moment.



Ex. Write the order of the dipole moment of following compounds ?

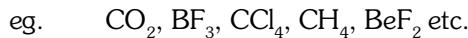


Sol. Right order is $\text{CCl}_4 < \text{CHCl}_3 < \text{CH}_2\text{Cl}_2 < \text{CH}_3\text{Cl}$
 $\mu = 0 \quad 1.02 \quad 1.55 \quad 1.93$

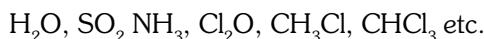
Applications of Dipole Moment

(a) To determine polarity and geometry of molecule :-

If $\mu = 0$ compound is non polar and symmetrical



If $\mu \neq 0$ compound will be polar and unsymmetrical.

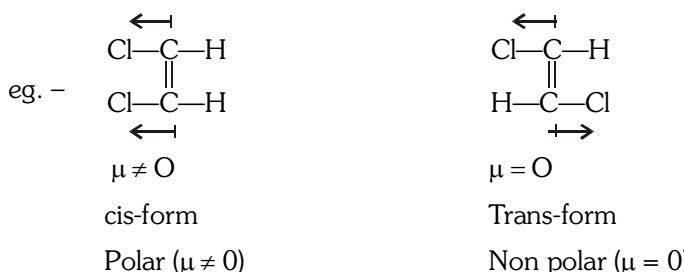


(b) To calculate % ionic character :-

$$\% \text{ Ionic character} = \frac{\text{Experimental value of } \mu}{\text{Theoretical Value of } \mu} \times 100$$

(c) To distinguish cis form or trans form :-

(I) Dipole moment of cis isomers is normally higher than trans isomers.



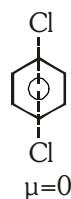
(II) If two groups have opposite inductive effect then trans-isomer will have greater dipole moment.



(d) To locate position of substituents in aromatic compounds.

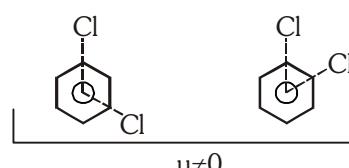
$$\mu \propto \frac{1}{\text{Bond angle}}$$

(I) If same substituents are present in the symmetrical position μ of benzene ring compounds will be zero.



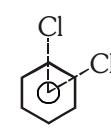
Angle 180°

p-dichloro benzene



Angle 120°

m-dichloro benzene



Angle 60°

o-dichloro benzene

(II) As angle between vector decreases value of μ increases.



Illustrations

Illustration 1. Calculate the μ of HCl ? If bond distance is 1.34 \AA , charge = $4.8 \times 10^{-10} \text{ esu}$ and calculate % ionic character if experimental value of $\mu = 1.08 \text{ D}$?

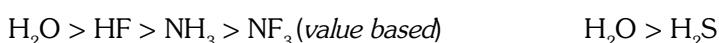
Solution $\mu = q \times d = 4.8 \times 10^{-10} \times 1.34 \times 10^{-8}$

$$\mu = 6.4 \times 10^{-18} \text{ esu cm.}$$

$$\% \text{ Ionic character} = \frac{1.08 \times 10^{-18}}{6.4 \times 10^{-18}} \times 100 = 16.79 \%$$

GOLDEN KEY POINTS

- **Some important orders of dipole moments :**



BEGINNER'S BOX-5

1. Which of the following contains polar and nonpolar bonds?

(1) H_2O_2 (2) CH_4 (3) HCN (4) NH_4Cl

2. Carbon tetrachloride has no net dipole moment because of-

(1) Similar electron affinity of C and Cl (2) its regular tetrahedral geometry
(3) its planar geometry (4) similar sizes of C and Cl atoms

3. Which of the following molecules is nonpolar?

(i) PbCl_4 (ii) BF_3 (iii) SnCl_2 (iv) CS_2
(1) (i), (ii), (iii) (2) (i), (ii), (iii), (iv) (3) (i), (ii), (iv) (4) (ii), (iii), (iv)

4. Which of the following has the highest dipole moment ?

(1) *o*-Dichlorobenzene (2) *m*-Dichlorobenzene (3) *p*-Dichlorobenzene (4) All have equal values

5. Both CO_2 and H_2O contain polar covalent bonds but CO_2 is nonpolar while H_2O is polar because-

(1) H atom is smaller than C atom
(2) CO_2 is a linear molecule while H_2O is an angular molecule
(3) O – H bond is more polar than C – H bond
(4) CO_2 contains multiple bonds while H_2O has only single bonds



2.10 MOLECULAR ORBITAL THEORY (MOT)

MOT put forward by Hund & Mulliken, which can be applied to explain the properties, which the old VBT (Valence bond theory) was unable to explain. eg. Paramagnetic nature of O_2 molecule, as per VBT ($:O = O:$) it should be diamagnetic.

Definition : The atomic orbital lose their identity during molecule formation (overlapping) and form new orbitals termed as molecular orbitals.

Characteristic of Molecular Orbitals

Comparison of Bonding molecular orbital & Antibonding molecular orbital:

Bonding molecular orbital(BMO)	Antibonding molecular orbital (ABMO)
<p>1. Bonding MO is the result of the linear combination of AO when their wave function are added</p> $\Psi_b = \Psi_A + \Psi_B$ <p>2. Generally it does not have nodal plane.</p> <p>3. Electron density increases between two nuclei resulting attraction between two atoms.</p> <p>4. Energy of BMO is less, hence stable.</p> <p>5. Electron placed in a BMO stabilises a molecule.</p>	<p>1. ABMO is result of linear combination of AO when their wave function are subtracted</p> $\Psi_a = \Psi_A - \Psi_B$ <p>2. It always have a nodal plane between two nuclei of bonded atom.</p> <p>3. Electron density decreases in between two nuclei, leads to repulsion between two atoms.</p> <p>4. Energy of ABMO is high.</p> <p>5. Electron placed in the ABMO destabilises the molecule.</p>

Notation of molecular orbitals

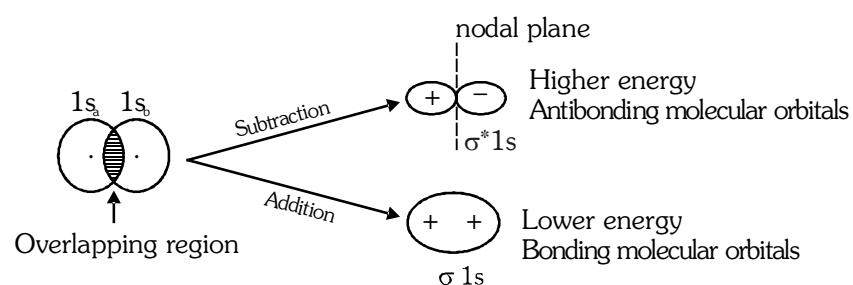
As atomic orbitals are known by letters s, p, d and f depending on their shapes. Similarly for molecular orbital For bonding molecular orbital - σ , π etc.

For antibonding molecular orbital- σ^* , π^* etc.

Shapes of Molecular Orbitals (L.C.A.O. Method)

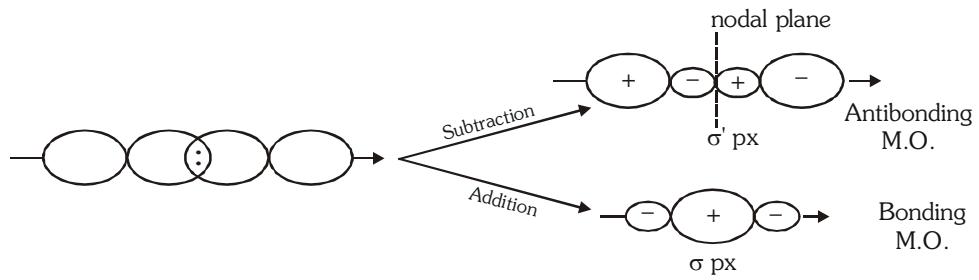
(A) (σ molecular orbital) :- It is formed by two ways -

(a) Combination of s-orbitals -



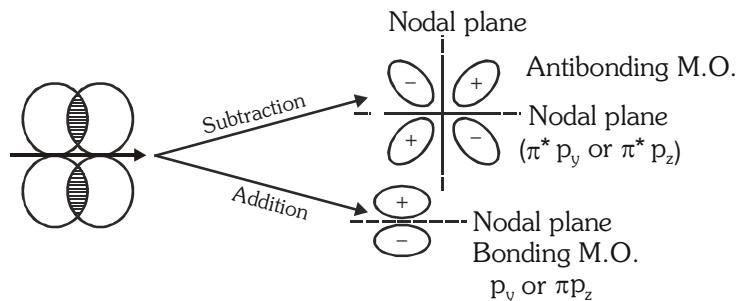
- σ^* 1s have one nodal plane

(b) End on overlapping of p-orbitals - (Linearly) :-



- $\sigma^* p_x$ have one nodal plane

(B) π (pi) molecular orbitals :-



Positive sign, represent maximum probability finding of electrons.

$\pi^* p_y$ or $\pi^* p_z$ have two nodal plane

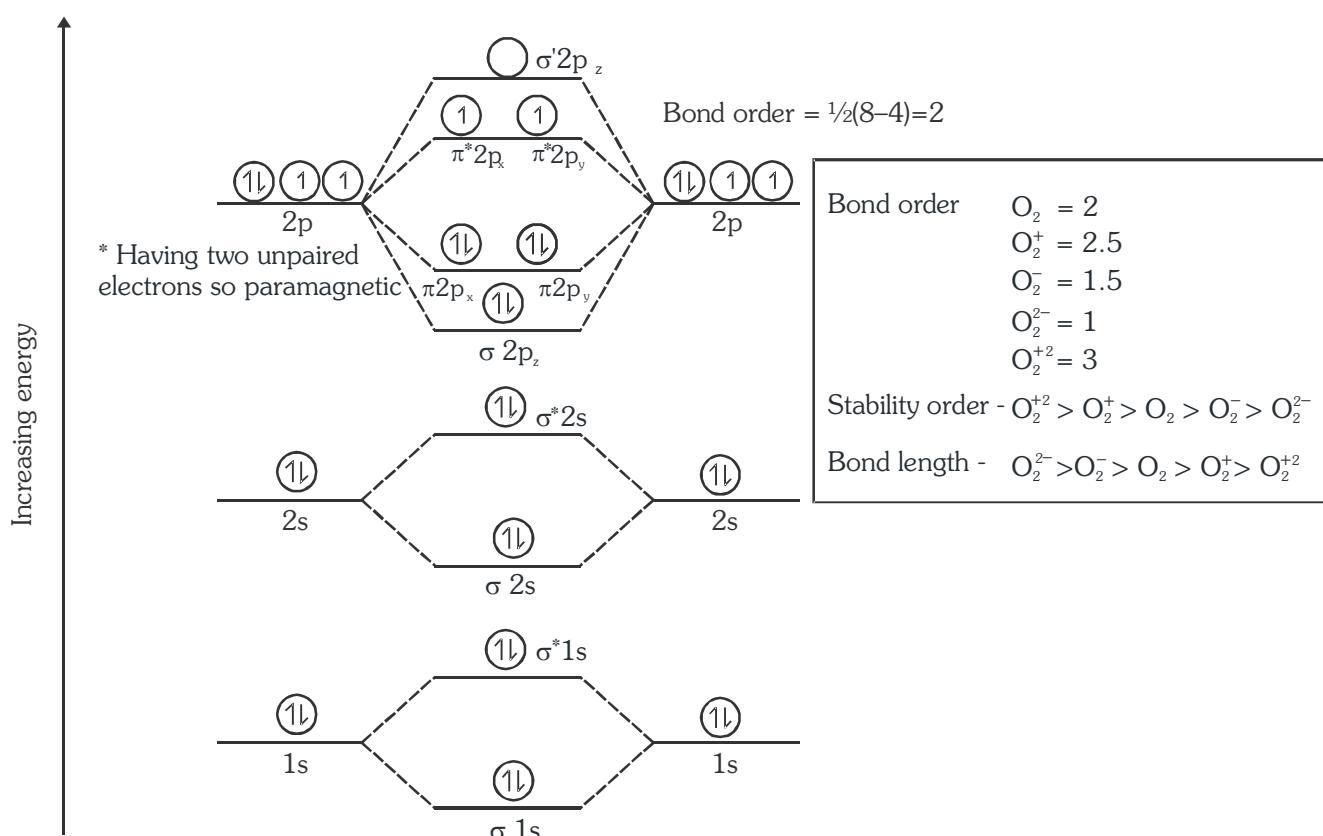
ENERGY LEVEL DIAGRAM OF MOLECULAR ORBITAL

(A) Energy level diagram for O_2, F_2, Ne_2 (Beyond N_2)

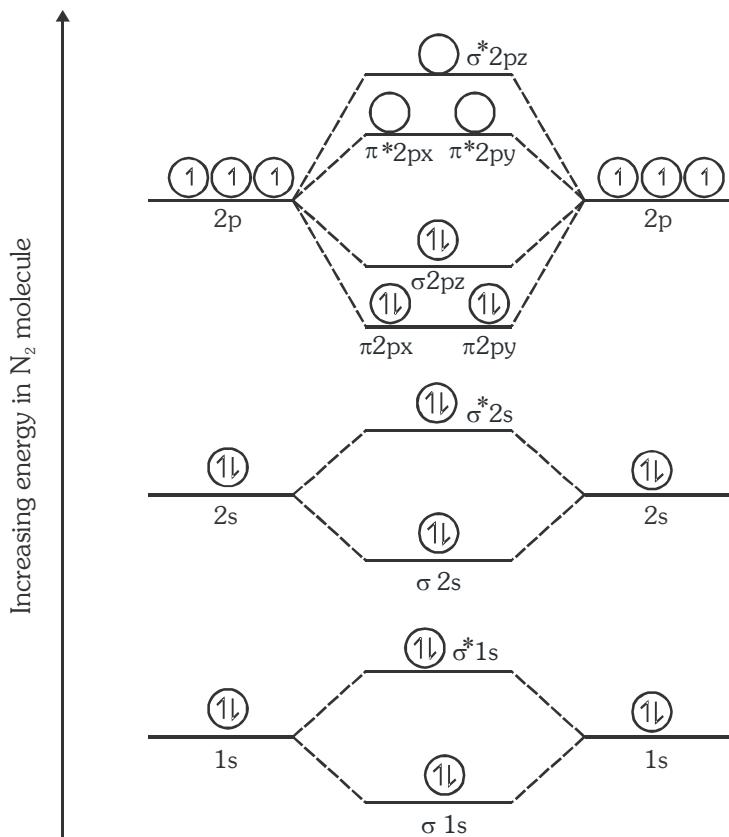
On the basis of Aufbau's rule - increasing order of energies of various molecular orbitals is -

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x \equiv \pi 2p_y < \pi^* 2p_x \equiv \pi^* 2p_y < \sigma^* 2p_z$

For O_2 molecule



(B) Energy level diagram for B_2 , C_2 and N_2 molecules (upto N_2)
 $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_x \equiv \pi 2p_y < \sigma 2p_z < \pi^* 2p_x \equiv \pi^* 2p_y < \sigma^* 2p_z$
For N_2 molecule



N_2 is diamagnetic in nature.
 Bond order of
 $N_2 = 3$
 $N_2^+ = 2.5$
 $N_2^- = 2.5$
 $N_2^{2-} = 2$
 Bond order
 $N_2 > N_2^+ \equiv N_2^- > N_2^{2-}$
 Bond length –
 $N_2^{2-} > N_2^- \equiv N_2^+ > N_2$
 But stability order
 $N_2 > N_2^+ > N_2^- > N_2^{2-}$

- Stability depends on number of electrons in antibonding molecular orbital if their bond order are same.
- Number of antibonding electrons increases, stability decreases.

Electronic configuration of molecules and their related properties :-

For writing electronic configuration of diatomic molecules following two rules to be followed-

- Count the number of electrons present in two atoms and then fill in the appropriate energy level diagram according to Aufbau rule.
- The pairing in $\pi 2p_x$ and $\pi 2p_y$ or $\pi^* 2p_x$ and $\pi^* 2p_y$ will take place only when each molecular orbital of identical energy has one electron.

GOLDEN KEY POINTS

- Bond order :-** $\frac{1}{2}[N_b - N_a]$ N_b = Total number of bonding electron
 N_a = Total number of antibonding electron

Application of bond order :

- Bond length :-** (distance between two nuclei) $\text{Bond length} \propto \frac{1}{\text{Bond order}}$

If	$N_b > N_a$	Molecule exists
$N_b < N_a$	}	Molecule do not exists
$N_b = N_a$		

- Stability of molecule :-** $\text{stability} \propto \text{Bond order of molecule}$
- Dissociation energy :-** $\text{Bond dissociation energy} \propto \text{Bond order.}$
- Magnetic property :-**

- When electron in MO are paired — diamagnetic
- When electron in MO are unpaired — paramagnetic



Bonding in molecules

(a) Hydrogen molecule

Having two H atoms with one electron each (1s)

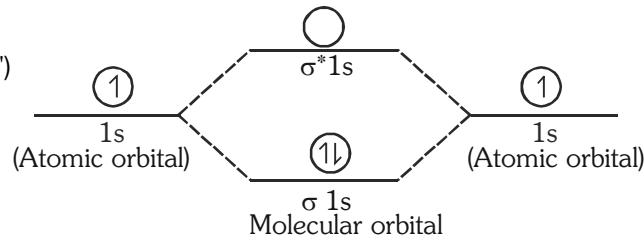
M.O. configuration of $H_2 = (\sigma 1s)^2 (\sigma^* 1s)^0$

Bond order = $\frac{1}{2} [N_b - N_a]$

= $\frac{1}{2} [2 - 0] = 1$ ie. single bond.

Having paired electron so diamagnetic.

Stability \rightarrow quite stable (having single bond)



(b) H_2^+ ion —

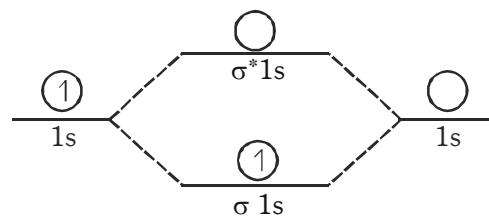
Configuration of $H_2^+ = (\sigma 1s)^1 (\sigma^* 1s)^0$

One electron in bonding molecular orbital.

So paramagnetic

Bond order = $\frac{1}{2}[1 - 0] = \frac{1}{2}$

Less stable. (In comparison to H_2)



(c) H_2^- anion -

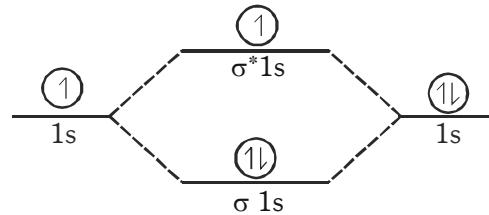
M.O. configuration - $(\sigma 1s)^2 (\sigma^* 1s)^1$

Paramagnetic

Bond order = $\frac{1}{2}[2 - 1] = \frac{1}{2}$

Stability is less than H_2^+ because H_2^-

contain an ABMO electron



Stability order $H_2 > H_2^+ > H_2^-$

Bond order 1.0 0.5 0.5

(d) Helium molecule (He_2)

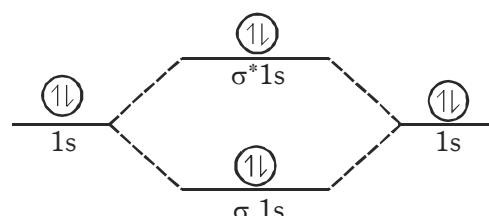
M.O. configuration - $(\sigma 1s)^2 (\sigma^* 1s)^2$

Diamagnetic

Bond order = $\frac{1}{2}[2 - 2] = 0$ (zero)

- Bond order zero indicates no linkage

between He atoms. Hence He_2 molecule does not exist.



Comparison between VBT and MOT

<ol style="list-style-type: none"> According to VBT electron moves around only one nucleus Orbitals are monocentric According to VBT O_2 is diamagnetic 	<ol style="list-style-type: none"> According to MOT electron moves under influence of two or more nuclei Orbitals are polycentric According to MOT O_2 is paramagnetic
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BEGINNER'S BOX-6

1. Which of the following is incorrect regarding the MO theory ?

- The number of molecular orbitals formed is always equal to the number of atomic orbitals combined.
- The more stable the bonding molecular orbital, the less stable the corresponding antibonding molecular orbital.
- In a stable molecule, the number of electrons in bonding molecular orbitals is always equal to that in antibonding molecular orbitals.
- Like an atomic orbital, each molecular orbital can accommodate up to two electrons with opposite spins in accordance with the Pauli exclusion principle.

2. If the z-axis is the molecular axis, then π MOs are formed by the overlap of–

(i) p_z and p_z	(ii) p_y and p_y	(iii) s_z and p_z	(iv) p_x and p_x
(1) (ii), (iv)	(2) (ii), (iii)	(3) (i), (ii)	(4) (i), (iii)

3. If the z-axis is taken as the internuclear axis, then which of the following combinations of atomic orbitals is a nonbonding combination ?

(1) s and p_y	(2) p_x and d_{yz}	(3) p_x and p_y	(4) all of these
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4. Which of the following is the correct order of stability ?

(1) $H_2 > H_2^+ > He_2 > He_2^+$	(2) $H_2 > He_2^+ > H_2^+ > He_2$	(3) $H_2 > H_2^+ > He_2^+ > He_2$	(4) $H_2 > He_2 > He_2^+ > He_2^+$
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5. Bond order in C_2^+ is:-

(1) $\frac{1}{2}$	(2) $\frac{2}{3}$	(3) $\frac{3}{2}$	(4) 1
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6. In which of the following set, the value of bond order will be 2.5:-

(1) O_2^+, NO, NO^{+2}, CN	(2) CN, NO^{+2}, CN^-, F_2
(3) $O_2^+, NO^{+2}, O_2^{+2}, CN^-$	(4) $O_2^{-2}, O_2^-, O_2^+, O_2$

7. Of the following species which has the highest bond order and shortest bond length :
 NO, NO^+, NO^{2+}, NO^-

- NO only
- Bond order of NO is highest and bond length of NO^{2+} is shortest
- NO^+ only
- NO^{2+} only

8. The diamagnetic molecule is

(1) Super oxide ion	(2) Oxygen molecule
(3) Carbon molecule	(4) Unipositive ion of nitrogen molecule

9. On the basis of molecular orbital theory which molecules does not exist

(1) H_2	(2) He_2	(3) HeH	(4) Li_2
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10. Maximum bond energy will be shown by the species

(1) O_2^+	(2) O_2	(3) O_2^-	(4) O_2^{-2}
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2.11 CO-ORDINATE BOND

(1) It is a covalent bond in which the shared e-pair come from one atom is called coordinate bond.

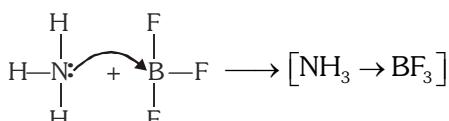
(2) Necessary conditions for the formation of coordinate bond are -

- Octet of donor atom should be complete and should have atleast one lone pair of electron.
- Acceptor atom should have deficiency of at least one pair of electron.

eg.: - $\ddot{\text{X}}\ddot{\text{Y}} \longrightarrow \begin{matrix} \text{x} & \text{x} \\ \text{x} & \text{x} \end{matrix}$ or $\text{X} \longrightarrow \text{Y}$

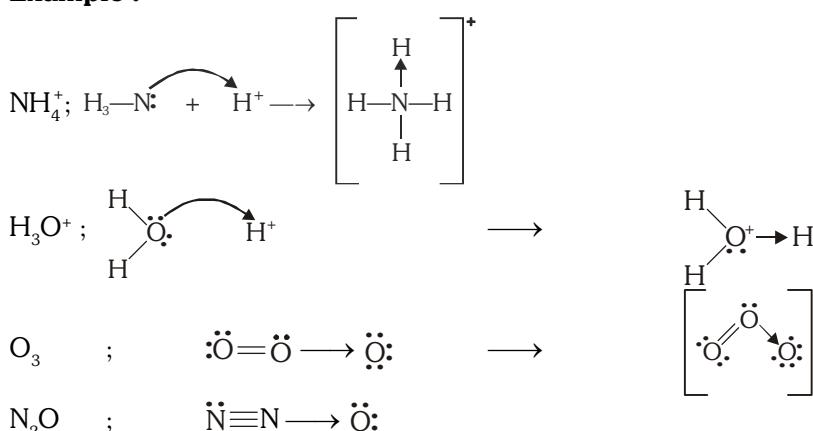
(3) Atom which provide electron pair for sharing is called donor.

(4) Other atom which accepts electron pair is called acceptor. That is why it is called donor-acceptor or dative bond.

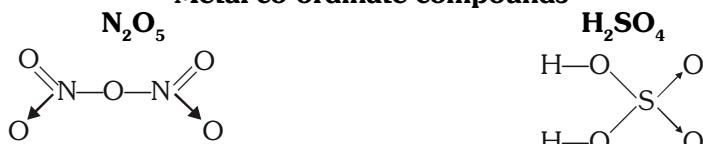


BF₃ is electron deficient compound.

Example :



Metal co-ordinate compounds :-



Compounds in which Ionic, covalent and co-ordinate bonds are present, are as follows -

NH_4Cl , CuSO_4 , $\text{K}_4[\text{Fe}(\text{CN})_6]$, Na_3PO_4 , KNO_3 , etc.

2.12 FORMAL CHARGE

The difference between the valence electrons in an isolated atom and the number of valence electrons assigned to that atom in a given Lewis structure is called that atom's formal charge. The formal charge, abbreviated FC, on an atom in a Lewis structure is given by the following relationship:

Formal charge on a atom in a Lewis structure

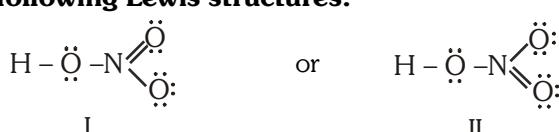
- (Total number of nonbonding electrons)

$$\text{or } \text{FC} = (\text{Valence electrons}) - (\text{Nonbonding electrons}) - \frac{1}{2} (\text{bonding electrons})$$

– (Valence electrons or group number) = [(Number of unshared e^- s) + (Number of bonds)]

To find the formal charge, we count the bonding electrons as though they are equally shared between the two bonded atoms.

Q. Calculate the formal charges on the various atoms of nitric acid (HNO_3) molecule which has been described by the following Lewis structures:



The H atom : It has one valence electron, zero lone pair (or zero nonbonding electrons), and forms one bond (two bonding electrons).

Substituting in Eq. (i), we write $FC = (1) - (0) - \frac{1}{2}(2) = 0$.

The O atom bonded to H: It has six valence electrons, two lone pairs (or four nonbonding electrons), and from two bonds (or four bonding electrons).

Hence, we write $FC = (6) - (4) - \frac{1}{2}(4) = 0$.

The N atom: It has five valence electrons, zero lone pair (or zero nonbonding electrons), and forms four bonds (or has eight bonding electrons).

Thus, we write $FC = (5) - (0) - \frac{1}{2}(8) = +1$

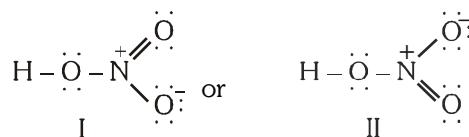
The end O atom in N = O: It has six valence electrons in the free state *but* in the Lewis structure (I or II), it has two lone pairs (or four nonbonding electrons) and forms two bonds (or has four bonding electrons).

Thus, we can write $FC = (6) - (4) - \frac{1}{2}(4) = 0$

The end O atom in N - O : It has six valence electrons in the free state but in the Lewis structure (I or II), it has three lone pairs or six nonbonding electrons and forms one bond (or has two bonding electrons).

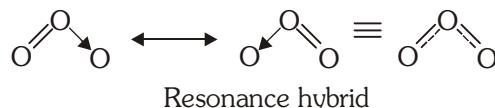
thus, we write $FC = (6) - (6) - \frac{1}{2}(2) = -1$

We can now write the Lewis structures (I and II) for nitric acid molecule including the formal charges as



2.13 RESONANCE

- (a) It has been found that the observed properties of certain compounds cannot be satisfactorily explained by writing a single lewis structure. The molecule is then supposed to have many structures, each of which can explain most of the properties of the molecule but none can explain all the properties of the molecules. The actual structure is in between of all these contributing structures and is called resonance hybrid and the different individual structures are called resonating structures or canonical forms. This phenomenon is called resonance.
- (b) Let us discuss resonance in ozone, according to its resonance structure it should have one single bond ($O-O = 1.48\text{\AA}$) but experiments show that both the bonds are same which can be proved by its resonance hybrid as shown below.



Note : To calculate bond order in the polyatomic molecule or ion use following formula :

$$\text{Bond order} = \frac{\text{Total number of bonds in a molecule}}{\text{Resonating Structures}}$$

Ex.	$O=C-O^-$	$C-O$	$\text{Bond order} = \frac{4}{3} = 1.33$
	$O=P-O^-$	$P-O$	$\text{Bond order} = \frac{5}{4} = 1.25$
	$O=Cl-O^-$	$Cl-O$	$\text{Bond order} = \frac{7}{4} = 1.75$



BEGINNER'S BOX-7

1. Which of the following ions has resonating structures ?

(1) SO_4^{2-} (2) PO_4^{3-} (3) SO_3^{2-} (4) All of these
2. How many resonating structures can be drawn for NO_2 ?

(1) Six (2) Four (3) Five (4) Two
3. Which of the following is true for nitrate anion

(1) Formal charge on N is zero (2) Bond order of NO bond is $\frac{4}{3}$
 (3) Average formal charge on oxygen is $-\frac{1}{3}$ (4) There are 2 π -bonds in the ion
4. Which of the following contains Co-ordinate and covalent bonds:-

(a) N_2H_5^+ (b) H_3O^+ (c) HCl (d) H_2O

Correct answer is :-

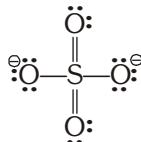
(1) a & d (2) a & b (3) c & d (4) Only a
5. The correct statement for the reaction –

$\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$:-

- (1) Hybridisation state is changed (2) Bond angle increases
- (3) NH_3 act as a Lewis acid (4) Regular geometry is changed

6. The number of coordinate bonds presents in SO_3 molecule are

(1) 1 (2) 2 (3) 3 (4) 4
7. One of the resonating structure of SO_4^{2-} is



Which set of formal charge on oxygen and bond order is correct

- (1) 0.5 and 1.5 (2) 1.5 and 3 (3) 2 and 3 (4) 1.5 and 1.5
8. Resonance is not shown by -

(1) C_6H_6 (2) CO_2 (3) CO_3^{2-} (4) SiO_2
9. Bond length of C – O is minimum in –

(1) CO (2) CO_2 (3) CO_3^{2-} (4) HCOO^-

Subjective Type Questions

10. Discuss resonance and formal charge in N_3^- and N_2O ?
11. Give the average formal charge and average bond order of XO bond in the following oxy compounds?

(a) SO_4^{2-} (b) SO_3^{2-} (c) NO_2^- (d) ClO_2^- (e) ClO_3^-
 (f) ClO_4^- (g) HCO_3^- (h) CO_3^{2-} (i) HSO_3^- (j) PO_4^{3-}



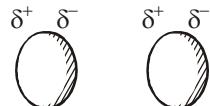
2.14 METALLIC BOND

- (1) The constituent particles of metallic solids are metal atoms which are held together by metallic bond.
- (2) In order to explain the nature of metallic bond Lorentz proposed a simple theory known as electron gas model or electron sea model.
- (3) A metal atom is supposed to consist of two parts, valence electrons and the remaining part (the nucleus and the inner shells) called kernel.
- (4) The kernels of metal atoms occupy the lattice sites while the space between the kernel is occupied by valence electrons.
- (5) Due to small ionisation energy the valence electrons or metal atoms are not held by the nucleus firmly. Therefore, the electrons leave the field of influence of one kernel and come under the influence of another kernel. Thus the electrons are not localised but are mobile.
- (6) The simultaneous attraction between the kernels and the mobile electrons which hold the kernel together is known as metallic bond.

WEAKER FORCES

2.15 Vander Waal's Forces

- (a) These are weak; non directional, non valence force of attraction among neutral species.
- (b) These are electrical in nature, due to induced polarity caused by temporary displacement of electrons towards one end of the inert atoms, becoming a temporary dipole.
- (c) This temporary dipole in one molecule can induce opposite dipoles in surrounding molecule due to displacement of electrons, one end becomes -ve and other +ve. These partially charged ends, induce surrounding molecules accordingly.
- (d) Strength of vander waal force depends on ease of distortion of electron cloud.



van der Waal's force \propto size of atom or molecule \propto atomic wt. or molecular weight.

- (e) Therefore m.p. and b.p. of noble gas elements (inert gas atom) and halogens increases down the group.

Types of van der Waal's Forces

(a) Keesom force or dipole dipole force - one dipole molecule orient the other dipole molecule, to bring opposite ends close to each other for attraction. This is called orientation effect. Example - HCl, H₂O, NH₃ etc.

(b) Debye force or dipole induce dipole force :- Forces which results from the interaction of a permanent dipole and induced dipole are called Debye force.

eg. When non-polar substance like benzene come in contact with polar molecules like NH₃, induced dipole moment in benzene appears (Induction effect).

(c) London dispersion force or Instantaneous dipole instantaneous induce dipole attraction :-

Due to vibration or moment to atom electron cloud and nuclei shifts temporarily towards opposite ends, leads to attraction between them, eg. In atoms of noble gases and halogens.



2.16 HYDROGEN BONDING

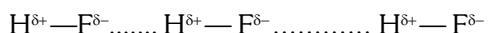
Definition

(a) It is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule and an electronegative atom.



X=F,O,N & sp carbon Y=F,O,N & Cl

- (b) It is not formed in ionic compounds.
- (c) H-bond forms in polar covalent compounds, (not in non-polar).
- (d) It is very weak bond but stronger than vander waal's force.
- (e) It is also known as dipole-dipole attraction.



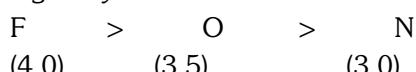
Main condition for H-bonding

- (a) H— should be covalently bonded with high electro –ve element like F, O, N.
- (b) Atomic size of electro –ve element should be small.

Order of atomic size is -

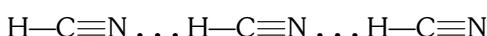


Order of electronegativity is -

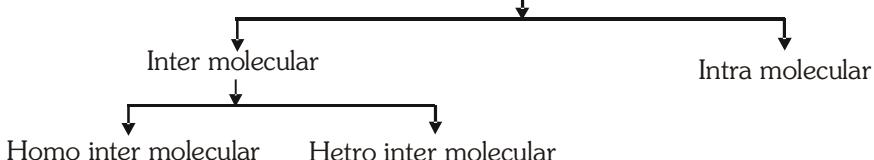


(c) Strength of H-bond \propto Electronegativity of Z (element) $\propto \frac{1}{\text{atomic size of Z}}$

(d) Hydrogen bonding occurs in HCN, due to ($\text{C} \equiv \text{N}$) triple bond (sp hybridisation), electronegativities of carbon and nitrogen increases.



TYPES OF HYDROGEN BONDING

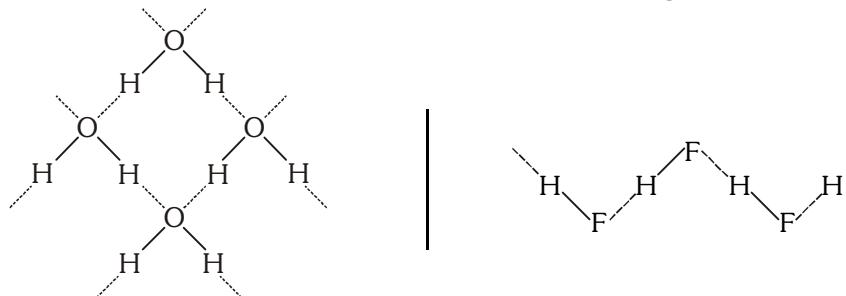


Intermolecular H-Bond

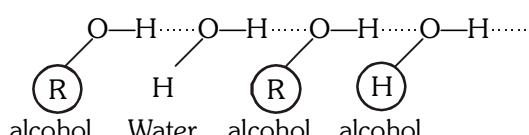
H-bond formation between two or more molecules of either the same or different compounds known as **Inter molecular H-bonding**.

These are of two types :-

(i) **Homo intermolecular** :- H-bond between molecules of same compound.



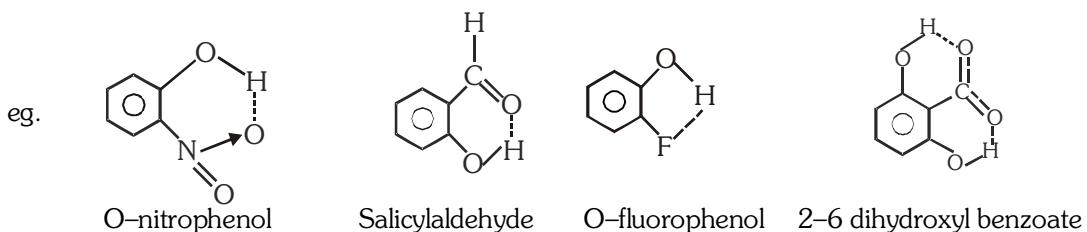
(ii) **Hetro intermolecular** :- H-bond between molecules of different compounds
Ex. between alcohol and water



Intramolecular H-bond

It takes place within the molecule.

- (a) H-bonded with electronegative element of a functional group, form H-bond with another electronegative element present on nearest position on the same molecule.
- (b) This type of H-bond is mostly occurred in organic compounds (Aromatic)
- (c) It results in ring formation (Chelation).



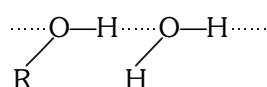
Effect of H-bond on Physical Properties

(A) Solubility

(a) Inter molecular H-bonding

- (I) Few organic compounds (Non-polar) are soluble in water (Polar solvent) due to H-bonding.

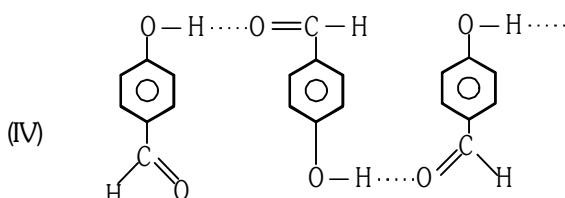
Ex. - Alcohol in water



Other examples - Glucose, Fructose etc. dissolve in water.

- (II) Ketone, ether, alkane etc. are insoluble (no H-bond). Dimethyl ether is soluble in water while diethyl ether is partially soluble, due to bulky ethyl groups H-bonding interrupts.

(III) Solubility order- $\text{CH}_3\text{OCH}_3 < \text{CH}_3\text{OH}$

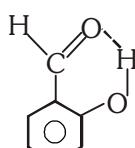


p-hydroxybenzaldehyde.

It can form H-bond with water molecule so it can dissolve.

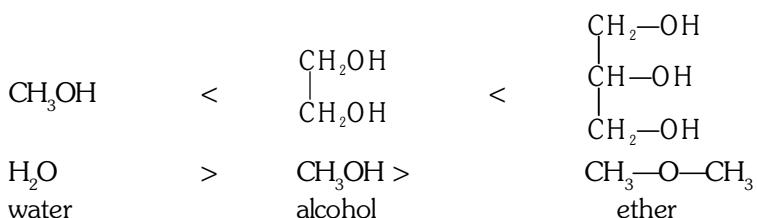
(b) Intra molecular H-bonding

- (I) It decreases solubility as it form chelate by H-bonding, so H- is not free for other molecule.
- (II) It can not form H-bond with water molecule so it can not dissolve.



(B) Viscosity

H-bond associates molecules together so viscosity increases.

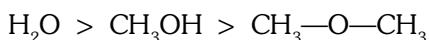


(C) Surface Tension

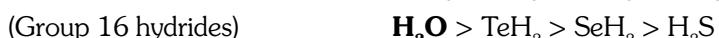
Surface tension of a liquid \propto extent of H-bonding.

(D) Melting point and boiling point

(I) Due to intermolecular H-bond M.P. & B.P. of compounds increases.



(II) Boiling points of VA, VIA, VIIA hydrides are as shown below :



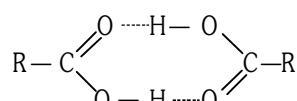
(III) But sudden increase in boiling point of NH_3 , H_2O and HF is due to H-bonding.

(IV) $\text{H}_2\text{O} > \text{HF} > \text{NH}_3$ (BP comparison due to combined effect of strength and number of H bond)

Intramolecular H-bonding gives rise to ring formation, so the force of attraction among these molecules are vander waal force. So M.P. and B.P. are low.

(E) Molecular weight

Molecular wt. of CH_3COOH is double of its molecular formula, due to dimer formation occur by H-bonding.



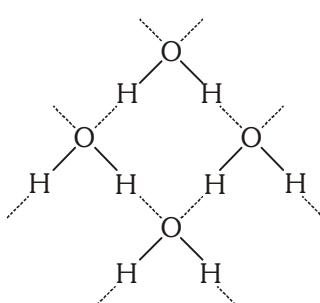
(F) Physical states

H_2O is liquid while H_2S is gas.

Water and Ice :- Both have H-bonding even then density of ice is less than water.

Volume of ice is more because of open cage like crystal structure, form by association of water molecules with the help of H-bond.

H_2O becomes solid due to four hydrogen bond among water molecule are formed in tetrahedral manner.

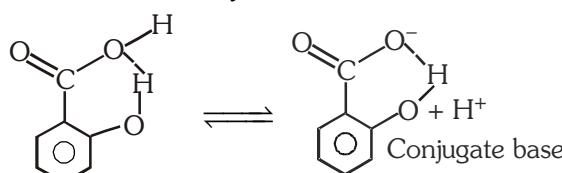


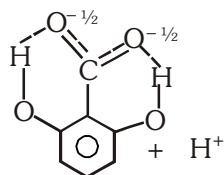
GOLDEN KEY POINTS

Effect of intramolecular H-bonding

• Strength of acid

(I) The formation of intramolecular H-bonding in the conjugate base of an acid gives extra stability to conjugate base and hence acid strength increases eg. Salicylic acid is stronger than benzoic acid
 $2, 6\text{-dihydroxy benzoic acid} > \text{salicylic acid} > \text{benzoic acid}$.



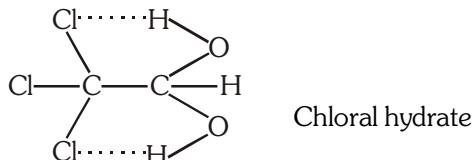


2, 6-dihydroxy benzoate ion.

(II) $\text{C}_2\text{H}_5\text{SH}$ is more acidic than $\text{C}_2\text{H}_5\text{OH}$. In $\text{C}_2\text{H}_5\text{OH}$, H-bond forms so H^+ is not free.
 (III) HF is weaker acid than HI, due to H-bond in H—F, H^+ is not free

● **Stability of chloral hydrate**

If two or more OH group on the same atom are present it will be unstable, but chloral hydrate is stable (due to H-bonding).



BEGINNER'S BOX-8

2.17 IONIC OR ELECTROVALENT BOND

The chemical bond formed between two or more atoms as a result of the complete transfer of one or more electrons from one atom to another is called Ionic or electrovalent bond.

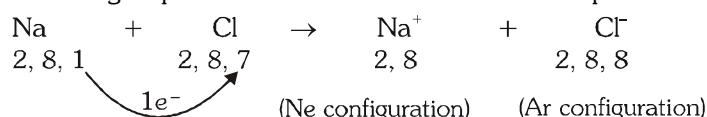
Electro +ve atom loses electron (group IA to IIIA)

Electro -ve atom gains electron (group VA to VIIA)

Electrostatic force of attraction between cation and anion is called ionic bond or electrovalent bond.

Nature of ionic bond \propto Electronegativity difference.

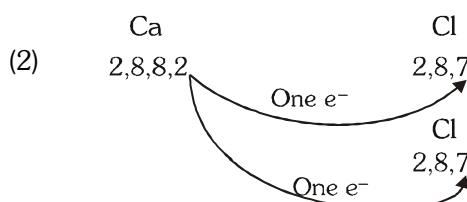
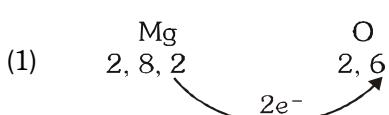
e.g. IA and VIIA group elements form maximum ionic compound.



More the distance between two elements in periodic table more will be ionic character of bond.

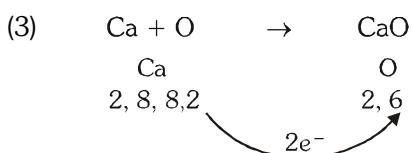
Total number of electron lose or gained is called electrovalency.

Example –



electrovalency of Mg = 2
electrovalency of O = 2

electrovalency of Ca = 2
electrovalency of Cl = 1



electrovalency of Ca = 2
electrovalency of O = 2

The force of attraction is equal in all direction so ionic bond is non-directional. A definite three dimensional structure is formed called crystal lattice. Energy released during the formation of one mole crystal lattice is called lattice energy.

Ionic compound do not have molecular formula. It has only empirical formula.

e.g. NaCl is empirical formula of sodium chloride

Conditions for Forming Ionic Bonds

Formation of Ionic bond depends upon these three factors –

(a) Ionisation energy :

Amount of energy required to remove an electron from the outermost orbit of an isolated gaseous atom to form the +ve ion or cation. (energy absorbed)

Lesser Ionisation energy \rightarrow Greater tendency to form cation.

e.g. $\text{Na}^+ > \text{Mg}^{+2} > \text{Al}^{+3}$ $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ } Cation formation tendency

(b) Electron affinity :

Amount of energy released when an electron is added to an isolated gaseous atom to form -ve ion (anion) energy released.

Higher electron affinity \rightarrow Greater tendency to form anion

$\text{Cl}^- > \text{F}^- > \text{Br}^- > \text{I}^-$ } Anion formation tendency
 $\text{F}^- > \text{O}^{-2} > \text{N}^{-3}$



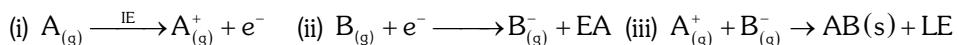
(c) **Lattice energy** - (Energy released) Amount of energy released when one mole of crystal lattice is formed

Higher lattice energy \rightarrow Greater will be the stability or strength of ionic compound.
or Amount of energy required to break the crystal.

(d) Overall lowering of energy :

Energy must be released during bond formation.

Energy changes are involved in the following steps —

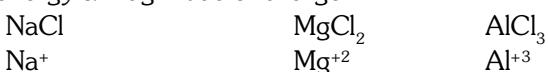


This concludes that for lower value of IE and higher value of EA there is more ease of formation of the ionic compound which is summarised as Born Haber Cycle.

GOLDEN KEY POINTS

● Factors affecting lattice energy

(1) Magnitude of charge $\rightarrow U \propto z^+ z^-$ (Ionic charge)
 Lattice energy \propto Magnitude of charge



- Lattice energy increases
- Charge of cation increases

(2) Size of Cation :- Lattice energy $\propto \frac{1}{r^+ + r^-}$



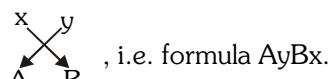
- Size of cation increasing
- Size of anion is constant
- Lattice energy decreases

● Representation of formula of compounds :

(1) Write the symbols of the ions side by side in such a way that positive ion is at the left and negative ion is at the right as A^+B^-

(2) Write their electrovalencies in figure at the top of each symbol as $A^x B^y$

(3) Now apply criss cross rule as



Examples : Calcium chloride

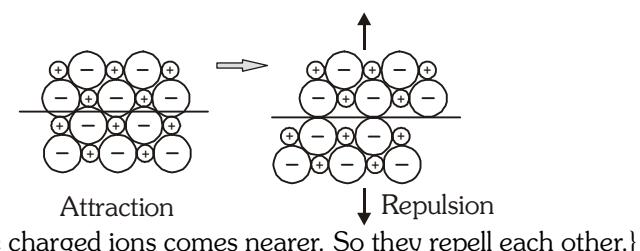


Properties of Ionic Compound

(a) Physical state –

Ionic compounds are hard, crystalline and brittle due to strong electrostatic force of attraction.

Brittleness →



(b) Isomorphism –

(1) Two compounds are said to be isomorphous if they have similar no. of electrons i.e. similar configuration of their cation and anion.

(2) They have similar crystal structure.

Example –

	Na ⁺	F ⁻	Mg ⁺²	O ⁻²
Valency	+1,	-1	+2,	-2
electronic configuration	2, 8	2, 8	2, 8	2, 8
similarly	Ca ⁺²	2Cl ⁻¹	2K ⁺¹	S ⁻²
	2, 8, 8	2, 8, 8	2, 8, 8	2, 8, 8
		2, 8, 8		2, 8, 8

(c) Boiling point and melting point –

Ionic compounds have high boiling point and melting point due to strong electrostatic force of attraction among oppositely charged ions.

(d) Conductivity –

It depends on ionic mobility. In solid state - No free ions - Bad conductor of electricity.

In fused state or aqueous solution Due to free ions - Good conductor of electricity.

Conductivity order Solid state < fused state < Aqueous solution

(e) Solubility –

Highly soluble in Polar solvents like water.

Less soluble in non polar solvents like benzene.

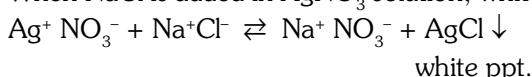
Ex. NaCl form a true solution in water but is colloid in benzene

(f) Ionic reaction –

(a) Ionic compounds shows ionic reaction and covalent compounds shows - molecular reaction.

(b) Ionic reactions are faster than molecular reaction because of free ions.

e.g. When NaCl is added in AgNO₃ solution, white ppt of AgCl is formed at once.



(g) Ionic bond non-directional and does not show stero isomerism

2.18 Polarisation (Fajan's Rule) (Covalent Nature in Ionic Bond)

When a cation approaches an anion closely the positive charge of a cation attract the electron cloud of the anion towards itself, due to the electrostatic force of attraction between them.

At the same time cation also repel the positively charge nucleus of anion.

Due to this combined effect, cloud of anion is bulged or elongated towards the cation. This is called distortion, deformation or Polarisation of the anion by the cation and anion is called Polarised.

Polarisation Power

The ability of cation to polarised a nearby anion is called Polarisation power of cation.



Polarizability

Ability of an anion to get polarised by the cation.

Polarisation of anion causes some sharing of electron between the ions so ionic bond acquires certain covalent character.

[Polarisation \propto Covalent character]

Magnitude of polarisation depends upon a no. of factors, suggested by Fajan and are known as Fajan's rule.



Fajan's Rule (Factors Affecting Polarisation)

(a) **Size of cation** : Polarisation of the anion increases as the size of cation decreases.

$$\text{Polarisation} \propto \frac{1}{\text{size of cation}}$$

eg. In a group



- Size of cation increases



- Covalent character decreases



- Ionic character increases



Greatest polarising power of Be^{2+} , shows its maximum covalent character

In a period — $\text{Na}^+, \text{Mg}^{+2}, \text{Al}^{+3}, \text{Si}^{+4}$

→

- Cation size decreases

- Covalent character increases

(b) **Size of anion** :- If the size of the anion increases for a given cation, the covalent character increases.
 $\text{Polarisation} \propto \text{size of anion}$.



- size of anion increases



- Covalent character increases



- Ionic character decreases

(c) **Charge on cation and anion** :-

$\text{Polarisation} \propto \text{charge on cation or anion}$

(i) **Polarisation (covalent character) \propto Charge on cation**

$$\text{eg. } \begin{array}{cccc} \text{NaCl} & \text{MgCl}_2 & \text{AlCl}_3 & \text{SiCl}_4 \\ \text{Na}^+ & \text{Mg}^{++} & \text{Al}^{+++} & \text{Si}^{++++} \end{array}$$

→

- Charge on cation increases

- Covalent character increases

- Ionic character decreases (M.P. decreases)

Ex. Write the increasing order of M.P. & B.P. of following compounds.

$$(1) \text{SnCl}_4, \text{SnCl}_2 \quad (2) \text{FeSO}_4, \text{Fe}_2(\text{SO}_4)_3 \quad (3) \text{PbCl}_4, \text{PbCl}_2$$

$$\text{Ans. } (1) \text{Sn}^{+4} < \text{Sn}^{+2} \quad (2) \text{Fe}^{+3} < \text{Fe}^{+2} \quad (3) \text{Pb}^{+4} < \text{Pb}^{+2}$$

(Charge on cation \propto polarisation power \propto covalent character $\propto \frac{1}{\text{M.P.}}$)

(ii) **Polarisation \propto Charge of anion**

$$\begin{array}{ccc} \text{F}^- & \text{O}^{2-} & \text{N}^{3-} \\ \hline & & \end{array}$$

- Charge increases

- Covalent character increases

$$\text{AlN} > \text{Al}_2\text{O}_3 > \text{AlF}_3$$



Charge on anion \propto polarisation \propto covalent nature $\propto \frac{1}{M.P.}$

(d) Electronic configuration of cation :-

Order of Polarisation power : $8e^- < (18+2)e^- < 18e^-$

$\text{CuCl} \longrightarrow \text{Cu}^+ \quad 2, 8, 18 \quad (\text{Covalent})$

$\text{NaCl} \longrightarrow \text{Na}^+ \quad 2, 8 \quad (\text{Ionic})$

Cu^+ and Na^+ both the cation (Pseudo inert & inert respectively) have same charge and size but polarising power of Cu^+ is more than Na^+ because -

$$\begin{array}{ccc} z_{\text{eff}} \text{ of } \text{ns}^2\text{p}^6 \text{ (inert)} & < & z_{\text{eff}} \text{ of } \text{ns}^2\text{p}^6\text{d}^{10} \text{ (pseudo inert)} \\ \text{Na}^+ & < & \text{Cu}^+ \\ (\text{Ionic}) & & (\text{Covalent}) \end{array}$$

So CuCl has more covalent character than NaCl .

Order of covalent character

- $\text{LiF} < \text{LiCl} < \text{LiBr} < \text{LiI}$
- $\text{CaCl}_2 < \text{FeCl}_2 < \text{FeCl}_3$
- $\text{SrCl}_2 < \text{SnCl}_2 < \text{CdCl}_2$
- $\text{SF}_2 < \text{SF}_4 < \text{SF}_6$
- $\text{Hg}_2\text{Cl}_2 < \text{HgCl}_2$
- $\text{ZnCl}_2 < \text{CdCl}_2 < \text{HgCl}_2$

Note :

Polarisation power of a cation is usually called ionic potential or charge density.

$$\text{Ionic potential } \phi \text{ (phi)} = \frac{\text{Charge on cation}}{\text{Size of cation}}$$

To determine covalent and ionic character of molecule

$$\phi \propto \frac{\text{Covalent Character}}{\text{Ionic character}}$$

From left (larger size) to right (smaller size) in a period ϕ increases so covalent character increases.

$$\begin{array}{cccc} \text{Na}^+, \quad \text{Mg}^{++} \quad \text{Al}^{+++} \quad \text{Si}^{++++} & \longrightarrow \\ - & \text{charge increases} & \left. \begin{array}{c} \\ \end{array} \right\} \phi \text{ increases} \\ - & \text{size decreases} & \left. \begin{array}{c} \\ \end{array} \right\} \phi \text{ increases} \\ - & \text{Covalent character increases} & \end{array}$$

From top to bottom in a group ϕ decreases so covalent character decreases.

Li^+	
Na^+	Size increases (charge is fix)
K^+	ϕ decreases
Rb^+	Hence covalent character decreases
Cs^+	



BEGINNER'S BOX-9

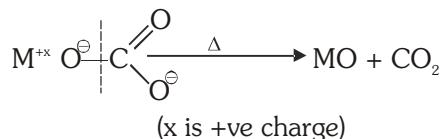
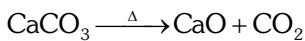
1. The electrovalency of the element is equal to the–
 - (1) number of electrons lost
 - (2) number of electrons gained
 - (3) number of electrons transferred
 - (4) number of electrons lost or gained by the atom of the element during the formation of ions of ionic compound
2. Which of the following polar solvents has the highest dielectric constant?
(1) H_2O (2) D_2O (3) CH_3OH (4) $\text{C}_2\text{H}_5\text{OH}$
3. Which of the following cations posses neither noble gas nor pseudo noble gas configurations?
(i) Bi^{3+} (ii) Pb^{2+} (iii) Sn^{2+} (iv) Tl^+
(1) (ii), (iii) (2) (i), (iv) (3) (i), (ii), (iii) (4) (i), (ii), (iii), (iv)
4. Ionic bond formation involves :
(1) Elimination of protons (2) Sharing of electrons
(3) Overlapping of orbitals (4) Formation of octets
5. The hydration of ionic compounds involves –
(1) Evolution of heat (2) Weakning of attractive forces
(3) Dissociation into ions (4) All
6. The hydration energy of Mg^{+2} is greater than the hydration energy of
(1) Al^{+3} (2) Mg^{+3} (3) Na^+ (4) Be^{+2}
7. Among the following which compounds will show the highest lattice energy ?
(1) KF (2) NaF (3) CsF (4) RbF
8. The lattice energy of the lithium is in the following order :
(1) $\text{LiF} > \text{LiCl} > \text{LiBr} > \text{LiI}$ (2) $\text{LiCl} > \text{LiF} > \text{LiBr} > \text{LiI}$
(3) $\text{LiBr} > \text{LiCl} > \text{LiF} > \text{LiI}$ (4) $\text{LiI} > \text{LiBr} > \text{LiCl} > \text{LiF}$
9. Among LiCl , BeCl_2 , BCl_3 and CCl_4 , the covalent bond character follows the order :
(1) $\text{LiCl} < \text{BeCl}_2 > \text{BCl}_3 > \text{CCl}_4$ (2) $\text{LiCl} > \text{BeCl}_2 < \text{BCl}_3 < \text{CCl}_4$
(3) $\text{LiCl} < \text{BeCl}_2 < \text{BCl}_3 < \text{CCl}_4$ (4) $\text{LiCl} > \text{BeCl}_2 > \text{BCl}_3 > \text{CCl}_4$



2.19 THERMAL DECOMPOSITION

Thermal stability of metal carbonates

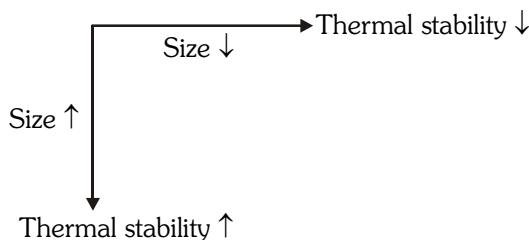
Thermal stability of compound having poly atomic anion



Polarising Power (\uparrow) Thermal Stability (\downarrow)

$$\text{Thermal stability} \propto \frac{1}{\text{Pol.power}} \propto \frac{\text{size of cation}}{\text{charge of cation}}$$

Compounds having poly atomic anions :



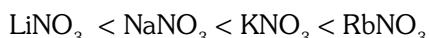
For fluoride, hydride & normal oxide

Thermal stability $\propto \frac{1}{\text{size}}$ for a group

[Thermal stability $\propto \Delta E_N$] for a period

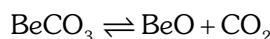
Thermal Stability order

For Example



Note :

- (i) LiHCO_3 and IIA group bicarbonate does not exist in solid state.
- (ii) Carbonate, Sulphates & hydroxide of Na, K, Rb & Cs do not decompose at high temperature only melt.
- (iii) BeCO_3 is kept in CO_2 atmosphere due to less thermal stability.



Heating Effect

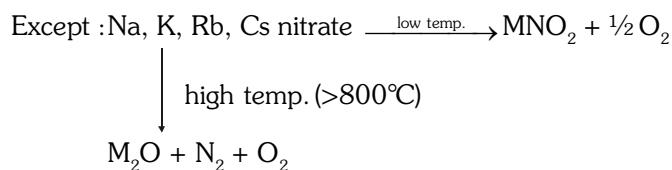
(a) Metal carbonate $\xrightarrow{\Delta}$ metal oxide + CO₂

(b) Metal hydroxide $\xrightarrow{\Delta}$ metal oxide + H₂O

(c) Metal bicarbonate $\xrightleftharpoons{\Delta}$ metal carbonate + CO₂ + H₂O

(d) Ammonium salts having CO₃⁻², PO₄⁻³, SO₄⁻², X-anion (non oxidising or weak oxidising) gives NH₃ gas on decomposition.
Ammonium salt having Cr₂O₇⁻², ClO₃⁻¹, NO₂⁻¹, NO₃⁻¹ (strong oxidising anion) gives N₂ or N₂O gas on decomposition.

(e) Metal nitrate $\xrightarrow{\Delta}$ metal oxide + NO₂ + O₂



Note :

(i) Some less stable metal oxide like Ag₂O & HgO further decompose into metal & oxygen.

(ii) Metal salts having high percentage of oxygen like KMnO₄, K₂Cr₂O₇ & KClO₃ give O₂ gas on decomposition.

Complete following reactions :

PbCO ₃ $\xrightarrow{\Delta}$	FeCO ₃ $\xrightarrow{\Delta}$
ZnCO ₃ $\xrightarrow{\Delta}$	MgCO ₃ · CaCO ₃ $\xrightarrow{\Delta}$
CuCO ₃ · Cu(OH) ₂ $\xrightarrow{\Delta}$	NaCO ₃ · 10H ₂ O $\xrightarrow{\Delta}$ X $\xrightarrow{\Delta}$
2NaHCO ₃ $\xrightarrow{\Delta}$	NH ₄ NO ₂ $\xrightarrow{\Delta}$
NH ₄ NO ₃ $\xrightarrow{\Delta}$	(NH ₄) ₂ SO ₄ $\xrightarrow{\Delta}$
(NH ₄) ₂ CO ₃ $\xrightarrow{\Delta}$	Ba(N ₃) ₂ or NaN ₃ $\xrightarrow{\Delta}$
Pb(NO ₃) ₂ $\xrightarrow{\Delta}$	Zn(NO ₃) ₂ $\xrightarrow{\Delta}$
Ca(NO ₃) ₂ $\xrightarrow{\Delta}$	LiNO ₃ $\xrightarrow{\Delta}$
NaNO ₃ $\xrightarrow{400^{\circ}\text{C}}$	PbCl ₄ $\xrightarrow{\Delta}$
FeCl ₃ $\xrightarrow{\Delta}$	AuCl ₃ $\xrightarrow{\Delta}$
CuSO ₄ · 5H ₂ O $\xrightarrow{<200^{\circ}\text{C}}$ A $\xrightarrow{>200^{\circ}\text{C}}$ B $\xrightarrow{800^{\circ}\text{C}}$	BaCl ₂ · 2H ₂ O $\xrightarrow{\Delta}$
ZnSO ₄ · 7H ₂ O $\xrightarrow{<200^{\circ}\text{C}}$ A $\xrightarrow{>200^{\circ}\text{C}}$ B $\xrightarrow{800^{\circ}\text{C}}$	AlCl ₃ · 6H ₂ O $\xrightarrow{\Delta}$
FeSO ₄ · 7H ₂ O $\xrightarrow{<200^{\circ}\text{C}}$ A $\xrightarrow{>200^{\circ}\text{C}}$ B $\xrightarrow{750^{\circ}\text{C}}$	CaCl ₂ · 6H ₂ O $\xrightarrow{\Delta}$
Fe ₂ (SO ₄) ₃ $\xrightarrow{\Delta}$	FeCl ₃ · 6H ₂ O $\xrightarrow{\Delta}$
CaSO ₄ · 2H ₂ O $\xrightarrow{<200^{\circ}\text{C}}$ A $\xrightarrow{>200^{\circ}\text{C}}$ B $\xrightarrow{\Delta}$	MgCl ₂ · H ₂ O $\xrightarrow{\Delta}$
2KMnO ₄ $\xrightarrow{\Delta}$	K ₂ Cr ₂ O ₇ $\xrightarrow{\Delta}$
2KClO ₃ $\xrightarrow{\Delta}$	(NH ₄) ₂ Cr ₂ O ₇ $\xrightarrow{\Delta}$



2.20 SOLUBILITY OF IONIC COMPOUNDS

(a) Solubility of ionic compounds :

Soluble in polar solvents like water which have high dielectric constant

Factors affecting solubility of ionic compounds :

(i) Dielectric constant of the solvent increases the solubility of compound increases



(ii) If heat of hydration of ions exceeds the lattice energy (L.E.) of ionic compounds, the ionic compounds will be soluble in water.

○ Lattice energy as well as hydration energy depend on the size of ions. Both lattice energy and hydration energy decrease with increase in ionic size.

Two general rule, regarding the solubility is that -

(a) If the anion and the cation are of comparable size, the cationic radius will influence the lattice energy. Since lattice energy decreases much more than the hydration energy with increasing ionic size, solubility will increase as we go down the group.



Solubility increases

(b) If the anion is large compared to the cation, (i.e. compound contain ions with widely different radii) the lattice energy will remain almost constant i.e. change is very small within a particular group. Since the hydration energies decrease down a group, solubility will decrease.



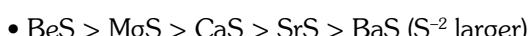
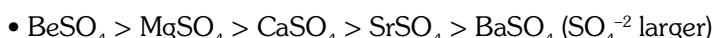
Solubility decreases

Note :

- If common ion is small like Na^+ , Li^+ , O^{2-} , F^- , OH^- , IIA cation then lattice energy dominates.
- If common ion is large like Cs^+ , Rb^+ , Br^- , I^- , polyatomic anion like CO_3^{2-} , SO_4^{2-} then hydration energy dominates.

Some important solubility orders:

Examples



Important facts about solubility

(i) All metal chlorides are soluble except Ag^+ , Pb^{2+} , Hg^{2+}

(ii) All metal sulphides are insoluble except : IIA and ammonium

(iii) Highly insoluble sulphides are of Hg^{2+} , Pb^{2+} , Cu^{2+} , Cd^{2+} , Bi^{3+}

(iv) All hydroxides are insoluble except IIA (Ca^{2+} , Sr^{2+} , Ba^{2+}) and ammonium

(v) Most insoluble hydroxides are of Al^{3+} , Fe^{3+} , Cr^{3+}

(vi) All metal nitrate, Acetate, perchlorate are soluble in water

(vii) Generally metal sulphates are soluble in water except Ag^+ , Hg^{2+} , Pb^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}

(viii) All alkali metal salts are soluble in water except . LiF , Li_2CO_3 , Li_3PO_4 , $\text{Li}_2\text{C}_2\text{O}_4$



2.21 MELTING POINT

Melting point of ionic compounds

The two factors which mainly influence the melting point of ionic compound are

(i) Lattice enthalpy (ii) Polarisation

$$\text{M.P.} \propto \text{LE when} \quad \left\{ \begin{array}{l} \text{Cation} = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+ \\ \text{or} \\ \text{Anion} = \text{F}^-, \text{O}^{2-}, \text{N}^{3-}, \text{C}^{4-}, \text{H}^+ \end{array} \right.$$

Melting point of ionic compound > covalent compound

Except Giant molecules



Diamond, Carborundum (SiC)
Norbide (B_4C), Silica (SiO_2) Borazone (BN_x)

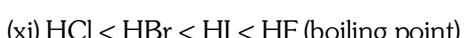
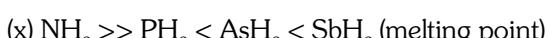
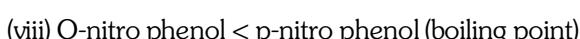
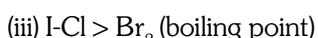
Order of Hardness : Diamond > Norbide > SiC > Al_2O_3

Some important melting point orders :

Examples



Melting Point and Boiling Point of non-metallic molecules



Melting point & boiling point of elements

(i) Li > Na > K > Rb > Cs (melting point)

(ii) Be > Ca > Sr > Ba > Mg (melting point)

3d series

Melting point \propto number of unpaired electrons

\therefore In 3d series (MP) maximum = Cr (chromium)

In 4d series (MP) maximum = Mo

In 5d series (MP) maximum = W

(iv) 3d < 4d < 5d (melting point)

(v) Zn > Cd > Hg (Melting point)

He < Ne < Ar < Kr < Xe (boiling point)

F₂ < Cl₂ < Br₂ < I₂ (boiling point)

N₂ < P₄ < As₄ (boiling point)

O₂ < S₈ < Se₈ < Te₈ (boiling point)

H₂ > He (melting point)

Note : Maximum melting point in Boron family \rightarrow Boron

Minimum melting point in Boron family \rightarrow Gallium

Maximum melting point in all elements \rightarrow Carbon

Minimum melting point in all elements \rightarrow Helium

Maximum melting point in Metals \rightarrow Tungsten

Minimum melting point in Metals \rightarrow Mercury

COLOUR OF COMPOUNDS

More the covalent character, more will be the colour intensity.

Colour intensity \propto ϕ (Covalent character)

Example :

AgF	AgCl	AgBr	AgI
(Colourless)	(White)	(Light yellow)	(Dark yellow)

 \rightarrow

BEGINNER'S BOX-10

Arrange in order of thermal stability :

1. BeCO₃ , MgCO₃ , CaCO₃ , SrCO₃ , BaCO₃

KO₂ , RbO₂ , CsO₂

NH₃ , PH₃ , AsH₃ , SbH₃ , BiH₃

H₂O , H₂S , H₂Se , H₂Te

BeO , MgO , CaO , SrO , BaO

NH₃ , H₂O , HF

NaF , MgF₂ , AlF₃

Na₂SO₄ , MgSO₄ , Al₂(SO₄)₃

CCl₄ , SiCl₄ , GeCl₄ , SnCl₄ , PbCl₄



2. Give solubility order for :-

- (i) alkali metal hydroxide
- (ii) Sodium halides
- (iii) alkali metal per chlorates
- (iv) alkali metal oxides
- (v) alkaline earth metal carbonates
- (vi) alkali metal carbonates
- (vii) alkali metal bicarbonates
- (viii) silver halides
- (ix) lead (II) halides
- (x) mercury (II) halides

3. Give the order of melting points

- Na_2O , MgO , Al_2O_3
- CaCl_2 , FeCl_2 , FeCl_3
- NaF , MgO , ScN , TiC
- SnCl_2 , SnCl_4
- KCl , CuCl , CuCl_2

ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	4					
	Ans.	3	4	2	1					

BEGINNER'S BOX-2	Que.	1	2	3	4	5	6	7	8	
	Ans.	3	1	4	3	1	3	1	2	

BEGINNER'S BOX-3	Que.	1	2	3	4	5	6	7	8	9	10	11
	Ans.	3	1	3	2	2	2	3	4	4	3	4

BEGINNER'S BOX-4	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	1	3	2	3	3	2	1	2	1	3

BEGINNER'S BOX-5	Que.	1	2	3	4	5				
	Ans.	1	2	3	1	2				

BEGINNER'S BOX-6	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	1	4	3	3	1	3	3	2	1

BEGINNER'S BOX-7	Que.	1	2	3	4	5	6	7	8	9	
	Ans.	4	4	2	2	2	2	1	4	1	

BEGINNER'S BOX-8	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	1	3	3	1	1	3	1	4	3

BEGINNER'S BOX-9	Que.	1	2	3	4	5	6	7	8	9	
	Ans.	4	1	4	4	4	3	2	1	3	



EXERCISE-I (Conceptual Questions)

OCTET RULE :

- Among the following element group number is not equals to valence electrons -

(1) Na	(2) N
(3) Ne	(4) None
- Which of the following does not act as lewis acid ?

(1) BF_3	(2) SnCl_4
(3) CCl_4	(4) SF_4

COVALENT BOND

- The strength of bonds by $2s - 2s$, $2p - 2p$ and $2p - 2s$ overlapping has the order :-

(1) $s - s > p - p > s - p$
(2) $s - s > p - s > p - p$
(3) $p - p > s - p > s - s$
(4) $p - p > s - s > p - s$
- In which of the excitation state of chlorine ClF_3 is formed:-

(1) In ground state
(2) In third excitation state
(3) In first excitation state
(4) In second excitation state
- A sigma bond is formed by the overlapping of :-

(1) $s - s$ orbital alone
(2) s and p orbitals alone
(3) $s - s$, $s - p$ or $p - p$ orbitals along internuclear axis
(4) $p - p$ orbital along the sides
- Which overlapping is involved in HCl molecule :-

(1) $s - s$ overlap	(2) $p - p$ overlap
(3) $s - d$ overlap	(4) $s - p$ overlap
- Which is not characteristic of π -bond:-

(1) π - bond is formed when a sigma bond already formed
(2) π - bond are formed from hybrid orbitals
(3) π - bond may be formed by the overlapping of p -orbitals
(4) π -bond results from lateral overlap of atomic orbitals

π bond is formed :-

(1) By overlapping of hybridised orbitals
(2) Overlapping of $s - s$ orbitals
(3) Head on overlapping of $p - p$ orbitals
(4) By $p - p$ collateral overlapping

Which of the following overlapping is strongest ?

(1) $1s - 1s$	(2) $2p - 2p$
(3) $2s - 2p$	(4) $1s - 2p$
- $p - p$ overlapping will be observed in the molecules of:

(1) Hydrogen	(2) Hydrogen bromide
(3) Hydrogen chloride	(4) Chlorine

- Which compound of xenon is not possible

(1) XeF_2 (2) XeF_4 (3) XeF_5 (4) XeF_6

- Similarity of fluorine and oxygen may not be attributed to-

(1) Their atomic and ionic radii are closely similar
(2) The atom of both elements attain an octet of electrons in their valence shell
(3) Both of them are highly electronegative elements
(4) Both form stable $p\pi - p\pi$ multiple bonds with themselves

- Higher is the bond order, greater is -

(1) Bond dissociation energy
(2) Covalent character
(3) Bond length
(4) Paramagnetism

HYBRIDISATION

- In the protonation of H_2O , change occurs in

(1) Hybridisation state of oxygen
(2) Shape of molecule
(3) Hybridisation and shape both
(4) None

- In the compound

$\overset{1}{\text{C}}\text{H}_2=\overset{2}{\text{C}}\text{H}-\overset{3}{\text{C}}\text{H}_2-\overset{4}{\text{C}}\text{H}_2-\overset{5}{\text{C}}\equiv\overset{6}{\text{C}}$, the $\text{C}^2 - \text{C}^3$ bond is formed by the overlapping of :-

(1) $sp - sp^2$	(2) $sp^3 - sp^3$
(3) $sp - sp^3$	(4) $sp^2 - sp^3$

- Among the following species identify the isostructural pairs:-

NF_3 , NO_3^- , BF_3 , H_3O^+ , HN_3

(1) $[\text{NF}_3, \text{NO}_3^-]$ and $[\text{BF}_3, \text{H}_3\text{O}^+]$
(2) $[\text{NF}_3, \text{HN}_3]$ and $[\text{NO}_3^-, \text{BF}_3]$
(3) $[\text{NF}_3, \text{H}_3\text{O}^+]$ and $[\text{NO}_3^-, \text{BF}_3]$
(4) $[\text{NF}_3, \text{H}_3\text{O}^+]$ and $[\text{HN}_3, \text{BF}_3]$

- Which of the set of species have same hybridisation state but different shapes:-

(1) NO_2^+ , NO_2^- , NO_2
(2) ClO_4^- , SF_4 , XeF_4
(3) NH_4^+ , H_3O^+ , OF_2
(4) SO_4^{2-} , PO_4^{3-} , ClO_4^-



18. Which of the following elements can not exhibit sp^3d hybridisation state:-
 (a) C (b) P (c) Cl (d) B
 Correct answer is:-
 (1) a, c (2) a, d (3) b, c (4) b, d

19. Which of the following species are expected to be planar:-
 (a) NH_3 (b) NH_3^{2+} (c) CH_3^+ (d) PCl_3
 The correct answer is:-
 (1) b and c (2) c and d
 (3) b and d (4) a and d

20. In which following set of compound/ion has linear shape
 (1) CH_4 , NH_4^+ , BH_4^- (2) CO_3^{2-} , NO_3^- , BF_3
 (3) NO_2^+ , CO_2 , XeF_2 (4) $BeCl_2$, BCl_3 , CH_4

21. Which order of decreasing bond angle is correct:-
 (1) $CCl_4 > BF_3 > NO_2^+$
 (2) $NH_3 > NCl_3 > NBr_3$
 (3) $Br_2O > Cl_2O > OF_2$
 (4) $PCl_3 > PBr_3 > PI_3$

22. Which of the following set is not correct:-
 (1) SO_3 , O_3 , NH_4^+ all have coordinate bonds
 (2) H_2O , NO_2 , ClO_2^- , all are 'V' shape molecules
 (3) I_3^- , ICl_2^- , NO_2^+ ; all are linear molecules
 (4) SF_4 , SiF_4 , XeF_4 are tetrahedral in shape

23. Shape of a molecule having 4 bond pairs and two lone pairs of electrons, will be :-
 (1) Square planar (2) Tetra hedral
 (3) Linear (4) Octa hedral

24. The shape of IF_4^+ will be :-
 (1) Square planar
 (2) Tetrahedral
 (3) Pentagonal bipyramidal
 (4) Distorted tetrahedral

25. Which of the following has pyramidal shape ?
 (1) BF_3 (2) H_3O^+
 (3) NO_3^- (4) CO_3^{2-}

26. A σ bonded molecule MX_3 is T-shaped. The number of non-bonding pairs of electrons is
 (1) 0
 (2) 2
 (3) 1
 (4) Can be predicted if atomic number of M is known.

27. Amongst CO_3^{2-} , AsO_3^{3-} , XeO_3 , ClO_3^- , BO_3^{3-} and SO_3^{2-} the non-planar species are :-
 (1) XeO_3 , ClO_3^- , SO_3^{2-} , AsO_3^{3-}
 (2) AsO_3^{3-} , XeO_3 , CO_3^{2-}
 (3) BO_3^{3-} , CO_3^{2-} , SO_3^{2-}
 (4) AsO_3^{3-} , BO_3^{3-} , CO_3^{2-}

28. The type of hybrid orbitals used by chlorine atom in ClO^- , ClO_2^- , ClO_3^- and ClO_4^- is/are :-
 (1) sp , sp^2 , sp^3 and sp^3d (2) sp and sp^3
 (3) Only sp^3 (4) only sp

29. On the basis of hybridization of one s & one p orbitals they are arranged at :-
 (1) Two orbitals mutually at 90° angle
 (2) two orbitals mutually at 180° angle
 (3) Two orbitals mutually at 120° angle
 (4) Two orbitals mutually at 150° angle

30. Which of the following having a square planar structure is
 (1) NH_4^+ (2) BF_4^- (3) XeF_4 (4) CCl_4

31. When p-character of hybridised orbital (formed by s and p orbitals) increases. Then the bond angle
 (1) Decreases (2) Increases
 (3) Becomes twice (4) Remains unaltered

32. Which orbitals overlap to form bond in OF_2
 (1) $sp^3 - 2p$ (2) $sp^2 - 2p$
 (3) $sp - 2p$ (4) $p - p$

33. In compounds X, all the bond angles are exactly $109^\circ 28'$. X is :
 (1) Chloromethane
 (2) Carbon tetrachloride
 (3) Iodoform
 (4) Chloroform

34. Among the following orbitals/bonds, the angle is minimum between :
 (1) sp^3 bonds
 (2) p_x and p_y orbitals
 (3) H—O—H bond in water
 (4) sp bonds

35. The structure and hybridization of $Si(CH_3)_4$ is :
 (1) bent, sp
 (2) trigonal, sp^2
 (3) octahedral, sp^3
 (4) tetrahedral, sp^3

36. The AsF_5 molecule is trigonal bipyramidal. The hybrid orbitals used by the As atoms for bonding are:
 (1) $d_{x^2-y^2}$, d_{z^2} , s, p_x , p_y (2) d_{xy} , s, p_x , p_y , p_z
 (3) s, p_x , p_y , p_z , d_{z^2} (4) $d_{x^2-y^2}$, s, p_x , p_y



37. When the hybridization state of carbon atom changes from sp^3 , sp^2 and sp , the angle between the hybridized orbitals.

- decrease considerably
- increase progressively
- decrease gradually
- all of these

38. The hybridization states of the central atoms of the ions I_3^- , ICl_4^- and ICl_2^- are respectively :

- sp^2 , dsp^2 , sp^3
- sp^3d , sp^3d^2 and sp^3d
- sp^3d , sp^3d , dsp^2
- sp , sp , dsp^2

39. Molecular shapes of SF_4 , CF_4 and XeF_4 are :-

- The same, with 2, 0 and 1 lone pairs of electrons respectively
- The same, with 1, 1 and 1 lone pairs of electrons respectively
- Different, with 0, 1 and 2 lone pairs of electrons respectively
- Different, with 1, 0 and 2 lone pairs of electrons respectively

40. Which of the following two are isostructural :-

- XeF_2 , IF_2^-
- NH_3 , BF_3
- CO_3^{2-} , SO_3^{2-}
- PCl_5 , ICl_5

41. Select the correct matching :

List I		List II	
A : XeF_4		1. Pyramidal	
B : XeF_6		2. T-shape	
C : XeO_3		3. Distorted octahedral	
D : $XeOF_2$		4. Square planar	
A	B	C	D
(1) 4	3	1	2
(2) 1	2	3	4
(3) 2	1	3	4
(4) 4	1	3	2

42. Which one of the following pair is a correct with respect to molecular formula of xenon compound and hybridization state of xenon in it :

- XeF_4 , sp^3
- XeF_2 , sp
- XeF_2 , sp^3d
- XeF_4 , sp^2

43. The xenon compound(s) that are iso-structural with IBr_2^- and BrO_3^- respectively are :

- Linear XeF_2 and pyramidal XeO_3
- Bent XeF_2 and pyramidal XeO_3
- Bent XeF_2 and planar XeO_3
- Linear XeF_2 and tetrahedral XeO_3

DIPOLE MOMENT

44. Which statement is correct:-

- All the compounds having polar bonds, have dipole moment
- SO_2 is non-polar
- H_2O molecule is non polar, having polar bonds
- PH_3 is polar molecule having non polar bonds

45. BeF_2 has zero dipole moment where as H_2O has a dipole moment because :-

- Water is linear
- H_2O is bent
- F is more electronegative than O
- Hydrogen bonding is present in H_2O

46. Which of the following species are symmetrical :-

- XeF_4
- XeF_6
- SO_2
- NH_3^{+2}

Correct answer is:-

- a and b
- b and c
- c and d
- a and d

47. Which of the following molecule have zero dipole moment:-

- BF_3
- CH_2Cl_2
- NF_3
- SO_2

48. The dipole moment of NH_3 is:-

- Less than dipole moment of NCl_3
- Higher than dipole moment of NCl_3
- Equal to the dipole moment of NCl_3
- None of these

49. Which of the following order of polarities of molecules is correct:-

- $HF > NH_3 > PH_3$
- $CH_4 > NH_3 > H_2O$
- $CH_3Cl < CH_2Cl_2 < CHCl_3$
- $BF_3 > BeF_2 > F_2$

50. Which set of molecules is polar :-

- XeF_4 , IF_7 , SO_3
- PCl_5 , C_6H_6 , SF_6
- $SnCl_2$, SO_2 , NO_2
- CO_2 , CS_2 , C_2H_6

51. Which of the following has symmetrical structure :

- PCl_3
- CH_2Cl_2
- $CHCl_3$
- CCl_4

52. Species having zero dipole moment :-

- XeF_4
- 1,2,4 trichloro benzene
- SF_4
- CH_2Cl_2



53. What conclusion can be drawn from the fact that BF_3 has no dipole moment but PF_3 does
 (1) BF_3 is not symmetrical but PF_3 is
 (2) BF_3 molecule must be linear
 (3) Atomic radius of P is larger than that of B
 (4) BF_3 molecule must be planar triangular

54. PCl_5 is non polar because :-
 (1) P – Cl bond is non-polar
 (2) Its dipole moment is zero
 (3) P – Cl bond is polar
 (4) P & Cl have equal electronegativity

55. Dipole moment of CO_2 is zero which implies that :
 (1) Carbon and oxygen have equal electronegativities
 (2) Carbon has no polar bond
 (3) CO_2 is a linear molecule
 (4) Carbon has bond moments of zero value

56. The correct order of dipole moment is :
 (1) $\text{CH}_4 < \text{NF}_3 < \text{NH}_3 < \text{H}_2\text{O}$
 (2) $\text{NF}_3 < \text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O}$
 (3) $\text{NH}_3 < \text{NF}_3 < \text{CH}_4 < \text{H}_2\text{O}$
 (4) $\text{H}_2\text{O} < \text{NH}_3 < \text{NF}_3 < \text{CH}_4$

57. Which of the following molecule does not possess a permanent dipole moment :
 (1) H_2S (2) SO_2 (3) SO_3^{2-} (4) CS_2

58. Which of the following has the highest value of dipole moment :
 (1) HCl (2) HF (3) HI (4) HBr

MOLECULAR ORBITAL THEORY

59. The ion that is isoelectronic with CO and having same bond order is :-
 (1) CN^- (2) O_2^+ (3) O_2^- (4) N_2^+

60. Which of the following is paramagnetic:-
 (1) O_2^- (2) CN^- (3) CO (4) NO^+

61. In the following which of the two are paramagnetic
 (a) N_2 (b) CO (c) B_2 (d) NO_2
 Correct answer is :-
 (1) a and c (2) b and c
 (3) c and d (4) b and d

62. The bond order of CO molecule on the basis of molecular orbital theory is
 (1) Zero (2) 2 (3) 3 (4) 1

63. The energy of $\sigma 2s$ orbital is greater, than $\sigma 1s^*$ orbital because
 (1) $\sigma 2s$ orbital is bigger than $\sigma 1s^*$ orbital
 (2) $\sigma 2s$ orbital is a bonding orbital whereas $\sigma 1s^*$ is an antibonding orbital
 (3) $\sigma 2s$ orbital has a greater value of n than $\sigma 1s^*$ orbital
 (4) None

64. The no. of antibonding electron pair in O_2^- is
 (1) 4 (2) 3
 (3) 8 (4) 10

65. Which of the following species will have the minimum bond energy
 (1) N_2 (2) N_2^-
 (3) N_2^+ (4) N_2^{-2}

66. Which of the following ion has not bond order of 2.5 ?
 (1) O_2^- (2) O_2^+
 (3) N_2^+ (4) N_2^-

67. In a homonuclear molecule which of the following set of orbitals are degenerate ?
 (1) σ_{2s} and σ_{1s} (2) π_{2p_x} and π_{2p_y}
 (3) π_{2p_x} and σ_{2p_z} (4) σ_{2p_z} and $\pi_{2p_x}^*$

COORDINATE BOND

68. In Co-ordinate bond, the acceptor atoms must essentially contain in its valency shell an orbital:-
 (1) With paired electron
 (2) With single electron
 (3) With no electron
 (4) With three electron

69. The bonds present in N_2O_5 are :-
 (1) Only ionic
 (2) Covalent & coordinate
 (3) Only covalent
 (4) Covalent & ionic

70. Dative bond is present in
 (1) SO_3 (2) NH_3
 (3) K_2CO_3 (4) BF_3

71. Which of the following has no coordinate bond ?
 (1) PH_3 (2) $\text{P}_2\text{H}_6^{+2}$
 (3) $\text{P}_2\text{H}_5^{\oplus}$ (4) PH_4^+

72. The compound containing co-ordinate bond is :
 (1) H_2SO_4 (2) O_3
 (3) SO_3 (4) All of these

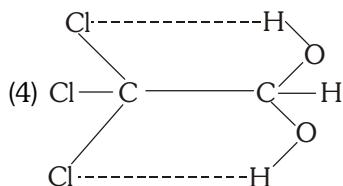
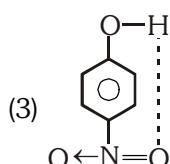
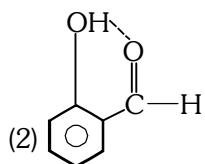
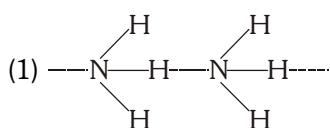
WEAK FORCES

73. In dry ice the bond present between two molecules is
 (1) Ionic bond (2) Covalent bond
 (3) Hydrogen bond (4) Vander Waal

74. Intermolecular hydrogen bonds are not present in:-
 (1) $\text{CH}_3\text{CH}_2\text{OH}$ (2) CH_3COOH
 (3) $\text{C}_2\text{H}_5\text{NH}_2$ (4) CH_3OCH_3



75. In which of the following molecule, the shown hydrogen bond is not possible:-



76. Correct order of volatility is:-
 (1) HF > HCl > HBr > HI
 (2) HCl > HBr > HI > HF
 (3) HI > HBr > HCl > HF
 (4) HBr < HCl < HI < HF

77. The correct order of volatility is:-
 (1) $\text{NH}_3 < \text{H}_2\text{O}$
 (2) p-nitro phenol < o-nitro phenol
 (3) $\text{CH}_3\text{OH} > \text{CH}_3-\text{O}-\text{CH}_3$
 (4) HF > HCl

78. The incorrect order of decreasing boiling points is
 (1) $\text{NH}_3 > \text{AsH}_3 > \text{PH}_3$ (2) $\text{H}_2\text{O} > \text{H}_2\text{Se} > \text{H}_2\text{S}$
 (3) $\text{Br}_2 > \text{Cl}_2 > \text{F}_2$ (4) $\text{CH}_4 > \text{GeH}_4 > \text{SiH}_4$

79. Acetic acid exists as dimer in benzene due to:-
 (1) Condensation reaction
 (2) Hydrogen bonding
 (3) Presence of carboxyl group
 (4) None of the above

80. Maximum no. of hydrogen bonds formed by a water molecule in ice is
 (1) 4 (2) 3
 (3) 2 (4) 1

81. Strongest hydrogen bond is shown by :
 (1) Water (2) Ammonia
 (3) Hydrogen fluoride (4) Hydrogen sulphide

82. Density of ice is less than that of water because of
 (1) presence hydrogen bonding
 (2) crystal modification of ice
 (3) open porous structure of ice due to hydrogen bonding
 (4) different physical states of these

83. NH_3 has abnormally high boiling point because it has :
 (1) Alkaline nature
 (2) Distorted shape
 (3) sp^3 - Hybridisation
 (4) Hydrogen bonding

84. Which of the following is soluble in water ?
 (1) CS_2 (2) $\text{C}_2\text{H}_5\text{OH}$
 (3) CCl_4 (4) CHCl_3

85. KF combines with HF to form KHF_2 . The compound contains the species :
 (1) K^+ , F^- and H^+ (2) K^+ , F^- and HF
 (3) K^+ and $[\text{HF}_2]^-$ (4) $[\text{KHF}]^+$ and F_2

86. Which of the following compounds show intramolecular hydrogen bonding :
 (A) o - nitrophenol
 (B) p - nitrophenol
 (C) phenol
 (D) salicylaldehyde
 (1) A & B (2) A & C
 (3) A & D (4) B & C

87. The pair of molecules forming strongest hydrogen bonds are :
 (1) SiH_4 and SiF_4
 (2) $\text{CH}_3-\overset{\text{O}}{\text{C}}-\text{CH}_3$ and CHCl_3
 (3) $\text{H}-\overset{\text{O}}{\text{C}}-\text{OH}$ and $\text{CH}_3-\overset{\text{O}}{\text{C}}-\text{OH}$
 (4) H_2O and H_2

IONIC BOND

88. Which one is the correct statement with reference to solubility of MgSO_4 in water:
 (1) Hydration energy of MgSO_4 is higher in comparison to its lattice energy
 (2) Ionic potential of Mg^{2+} is very low
 (3) SO_4^{2-} ion mainly contributes towards hydration energy
 (4) Size of Mg^{2+} and SO_4^{2-} are similar



89. Conditions for ionic bond formation is/are :
 (a) Small cation, large anion
 (b) Low IP of cation, high electron affinity of anion
 (c) Large cation, small anion and less charge
 (d) Less lattice energy
 Correct answer is:
 (1) a, d (2) b, c and d
 (3) b and c (4) a, b

90. Capacity of solvent to neutralise charge on ionic compound is called:-
 (1) Solvation energy (2) Dielectric constant
 (3) Dipole moment (4) Solubility

91. The force responsible for dissolution of ionic compound in water is –
 (1) Dipole – dipole forces
 (2) Ion – dipole force
 (3) Ion – ion force
 (4) Hydrogen bond

92. Born Haber cycle is mainly used to determine
 (1) Lattice energy (2) Electron affinity
 (3) Ionisation energy (4) Electronegativity

93. An ionic compound $A^+ B^-$ is most likely to be formed when –
 (1) Ionization energy of A is low
 (2) Electron affinity of B is high
 (3) Electron affinity of B is low
 (4) Both (1) and (2)

94. The pair of elements which on combination are most likely to form an ionic compound is
 (1) Na and Ca (2) K and O
 (3) O and Cl (4) Al and I

95. Choose the compound of each of the following pairs that has the more solubility in water :-
 (a) $BeSO_4$, $BaSO_4$ (b) $NaCl$, $MgCl_2$
 (c) $AgCl$, AgI
 (1) $BeSO_4$, $MgCl_2$, AgI (2) $BeSO_4$, $NaCl$, $AgCl$
 (3) $BaSO_4$, $NaCl$, $AgCl$ (4) $BaSO_4$, $MgCl_2$, AgI

96. Highest melting point would be of
 (1) $AlCl_3$ (2) $LiCl$
 (3) $NaCl$ (4) $BeCl_2$

97. Which of the following substance will have highest b.p.t. ?
 (1) He (2) CsF
 (3) NH_3 (4) $CHCl_3$

98. As compared to covalent compounds electrovalent compounds generally possess
 (1) High m.p. and high b.p.
 (2) Low m.p. and low b.p.
 (3) Low m.p. and high b.p.
 (4) high m.p. and low b.p.

99. The electronic configuration of metal M is $1s^2 2s^2 2p^6 3s^1$. The formula of its oxide will be :
 (1) MO (2) M_2O
 (3) M_2O_3 (4) MO_2

100. Which of the following pairs will form the most stable ionic bond ?
 (1) Na and Cl (2) Mg and F
 (3) Li and F (4) Na and F

101. For two ionic solids, CaO and KI . Identify the wrong statement among the following :
 (1) Lattice energy of CaO is much larger than that of KI
 (2) KI is soluble in benzene
 (3) CaO has higher melting point
 (4) KI has lower melting point

102. Which of the following does not show electrical conduction ?
 (1) diamond
 (2) graphite
 (3) sodium chloride (fused)
 (4) potassium

103. The most covalent halide is:-
 (1) AlF_3 (2) $AlCl_3$
 (3) $AlBr_3$ (4) AlI_3

104. Ionic potential (ϕ) of electropositive element will be highest in which of the following compound:-
 (1) $CsCl$ (2) $MgCl_2$
 (3) AlF_3 (4) SF_6

105. $LiCl$ is soluble in organic solvent while $NaCl$ is not because :-
 (1) Lattice energy of $NaCl$ is less than that of $LiCl$
 (2) Ionisation potential of Li is more than that of Na
 (3) Li^+ has more hydration energy than Na^+ ion
 (4) $LiCl$ is more covalent compound than that $NaCl$

106. The most stable carbonate is
 (1) Li_2CO_3 (2) $BeCO_3$
 (3) $CaCO_3$ (4) $BaCO_3$

107. Correct order of covalent character of alkaline earth metal chloride in
 (1) $BeCl_2 < MgCl_2 < CaCl_2 < SrCl_2$
 (2) $BeCl_2 < CaCl_2 < SrCl_2 < MgCl_2$
 (3) $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2$
 (4) $SrCl_2 > BeCl_2 > CaCl_2 > MgCl_2$

108. Which of the compound is least soluble in water
 (1) AgF (2) $AgCl$
 (3) $AgBr$ (4) AgI



109. CCl_4 is more covalent than LiCl because :

- There is more polarization of Cl in CCl_4
- There is more polarization of Cl in LiCl
- CCl_4 has more weight
- None of above

110. The M.P. of SnCl_4 is less than that of SnCl_2 , the suitable reason for the observed fact is

- There is more charge on Sn^{+4}
- The size of Sn^{+4} is small
- Ionic potential of Sn^{+4} is high
- The shape of SnCl_4 is tetrahedral

111. The correct order of decreasing polarisable ions is:

- Cl^- , Br^- , I^- , F^-
- F^- , I^- , Br^- , Cl^-
- F^- , Cl^- , Br^- , I^-
- I^- , Br^- , Cl^- , F^-

112. Ionic conductances of hydrated M^+ ions are in the order –

- $\text{Li}^+(\text{aq}) > \text{Na}^+(\text{aq}) > \text{K}^+(\text{aq}) > \text{Rb}^+(\text{aq}) > \text{Cs}^+(\text{aq})$
- $\text{Li}^+(\text{aq}) > \text{Na}^+(\text{aq}) < \text{K}^+(\text{aq}) < \text{Rb}^+(\text{aq}) < \text{Cs}^+(\text{aq})$
- $\text{Li}^+(\text{aq}) > \text{Na}^+(\text{aq}) > \text{K}^+(\text{aq}) > \text{Rb}^+(\text{aq}) < \text{Cs}^+(\text{aq})$
- $\text{Li}^+(\text{aq}) < \text{Na}^+(\text{aq}) < \text{K}^+(\text{aq}) < \text{Rb}^+(\text{aq}) < \text{Cs}^+(\text{aq})$

113. Which of the following halides has the highest melting point –

- NaCl
- KCl
- NaBr
- NaF

114. Which of the following does not give an oxide on heating –

- MgCO_3
- Li_2CO_3
- ZnCO_3
- K_2CO_3

115. Which decomposes on heating –

- NaOH
- KOH
- LiOH
- RbOH

116. Which of the following forms metal oxide on heating

- Na_2CO_3
- Li_2CO_3
- K_2SO_4
- NaHCO_3

117. Increasing order of stability of –

I. K_2CO_3	II. MgCO_3	III. Na_2CO_3
(1) I < II < III	(2) II < III < I	(3) II < I < III
(4) I < III < II		

118. Which of the following carbonate will not decompose on heating :-

- BaCO_3
- ZnCO_3
- Na_2CO_3
- Li_2CO_3

119. The decomposition temperature is maximum for:-

- BeCO_3
- CaCO_3
- K_2CO_3
- Li_2CO_3

EXERCISE-I (Conceptual Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	3	3	3	3	4	2	4	1	4	3	4	1	2	4
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	3	3	2	1	3	3	4	1	4	2	2	1	3	2	3
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	1	1	2	2	4	3	2	2	4	1	1	3	1	4	2
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	4	1	2	1	3	4	1	4	2	3	1	4	2	1	1
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Ans.	3	3	3	2	4	1	2	3	2	1	1	4	4	4	3
Que.	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
Ans.	2	2	4	2	1	3	3	4	2	3	3	3	1	3	2
Que.	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105
Ans.	2	1	4	2	2	3	2	1	2	2	2	1	4	4	4
Que.	106	107	108	109	110	111	112	113	114	115	116	117	118	119	
Ans.	4	3	4	1	3	4	4	4	4	3	2	2	3	3	



95. Which pair not shows same shape :-
 (1) I_3^{-1} , BeCl_2 (2) BF_3 , ClO_3^{-1}
 (3) SO_2 , H_2O (4) XeF_4 , BrF_4^{-}

96. In which at least one σ -bond of np (σ_{np}) orbital is present :-
 (1) B_2 (2) O_2
 (3) C_2 (4) Li_2

97. Which is correct for dipole moment :-
 (1) $\text{NH}_3 < \text{NF}_3$ (2) $\text{SO}_2 < \text{SO}_3$
 (3) $\text{NF}_3 > \text{BF}_3$ (4) $\text{SO}_2 > \text{H}_2\text{O}$

98. Which of the following is a molecular solid :-
 (1) solid SO_2 (2) SiC
 (3) C. (graphite) (4) ZnS

99. The geometry and No. of lone pair on ClF_2^- and ClF_4^- are respectively :-
 (1) Square planar, 2 & Linear, 3
 (2) Square Planar, 3 & Linear, 2
 (3) Linear, 3 & Square planar, 2
 (4) Tetrahedral, 2 & linear, 3

100. Wrong statement for N_3^- is :-
 (1) Isoelectronic with CO_2
 (2) Structure is linear
 (3) Both N-N bond lengths are unequal in hydrogen azide
 (4) Oxidation state for Nitrogen is same as in NH_2OH

101. Bond order of which of following pair is different:-
 (1) F_2^- & O_2^{-2} (2) N_2^- & O_2^+
 (3) C_2 & B_2^{-2} (4) N_2 & O_2^{2+}

102. Correct order for Bond angle is
 (1) $\text{SO}_2 > \text{NH}_3$ (2) $\text{NH}_3 < \text{H}_2\text{O}$
 (3) $\text{SO}_2 < \text{H}_2\text{O}$ (4) $\text{H}_2\text{S} > \text{NH}_3$

103. Which of the following two species have same shape but different hybridisation
 (1) XeF_2 and ICl_2^- (2) NO_2^+ and SO_2
 (3) BeCl_2 and NO_2^+ (4) SO_2 and NH_2^-

104. Which of the following has maximum %s character in N-H bond ?
 (1) N_2H_2 (2) NH_4^+ (3) NH_3 (4) N_2H_4

EXERCISE-II (Previous Year Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	2	4	2	3	2	1	3	3	1	2	2	2	4	1	3
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	1	2	4	1	3	3	3	4	2	2	1	1	3	1	1
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	1	2	2	3	4	3	2	3	3	4	3	3	1	1	3
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	2	3	3	3	1	4	2	1	3	2	4	2	2	1	3
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Ans.	4	2	2	1	1	2	1	1	4	2,3	1	2	2	2	2
Que.	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
Ans.	2	2	3	3	1	2	3	2	3	3	3	4	1	4	2
Que.	91	92	93	94	95	96	97	98	99	100	101	102	103	104	
Ans.	3	2	4	4	2	2	3	1	3	4	1	1	4	1	



Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

(A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.

(B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.

(C) If Assertion is True but the Reason is False.

(D) If both Assertion & Reason are false.

1. **Assertion** : Ionic bonds are formed between metal and nonmetals
Reason : In ionic bonds electrons are shared
(1) A (2) B (3) C (4) D

2. **Assertion** : D_2O is better solvent for ionic compounds, than H_2O .
Reason : dielectric constant of D_2O is higher than H_2O .
(1) A (2) B (3) C (4) D

3. **Assertion** : Hydrated ionic radius of Li^+ is maximum in IA group elements.
Reason : Lithium is a metal
(1) A (2) B (3) C (4) D

4. **Assertion** : $LiCl$ exhibits covalent character.
Reason : Lithium is lightest metal.
(1) A (2) B (3) C (4) D

5. **Assertion** : K_2CO_3 do not gives CO_2 gas on heating.
Reason : Value of $\sqrt{\phi}$ for K^+ is high.
(1) A (2) B (3) C (4) D

6. **Assertion** : CO_2 molecule is non-polar while SO_2 is polar.
Reason : Carbon atom is smaller than sulphur.
(1) A (2) B (3) C (4) D

7. **Assertion** : CH_3OH is soluble in water
Reason : CH_3OH is ionic in nature
(1) A (2) B (3) C (4) D

8. **Assertion** : Boiling point of H_2O is greater than C_2H_5OH .
Reason : Molecular wt. of H_2O is higher than C_2H_5OH .
(1) A (2) B (3) C (4) D

9. **Assertion** : NO^+ is more stable than NO^- .
Reason : NO^+ do not have electron in antibonding orbitals.
(1) A (2) B (3) C (4) D

10. **Assertion** : In MgO electrovalency of Mg is 2.
Reason : Mg shares two electrons with oxygen.
(1) A (2) B (3) C (4) D

11. **Assertion** : Ionic reactions are faster than molecular reactions.
Reason : Ionic bonds are weaker than covalent bonds.
(1) A (2) B (3) C (4) D

12. **Assertion** : LiI is more soluble in water than LiF .
Reason : LiI has more ionic character.
(1) A (2) B (3) C (4) D

13. **Assertion** : Bond energy of H–H bond is greater than Cl–Cl bond.
Reason : H_2 is more covalent than Cl_2 .
(1) A (2) B (3) C (4) D

14. **Assertion** : Ionic compounds tend to be non-volatile.
Reason : Inter ionic forces in these compounds are strong.
(1) A (2) B (3) C (4) D

15. **Assertion** : NCI_3 has pyramidal shape
Reason : In NCI_3 central atom is sp^3 hybridised.
(1) A (2) B (3) C (4) D

16. **Assertion** : BF_3 is planar while NF_3 is non-planar molecule.
Reason : B–F bond is more polar than N–F bond.
(1) A (2) B (3) C (4) D

17. **Assertion** : Density of ice is greater than water
Reason : In ice H_2O molecules are closely packed.
(1) A (2) B (3) C (4) D

18. **Assertion** : Bond order of O_2 and BN is same.
Reason : O_2 and BN are isoelectronic
(1) A (2) B (3) C (4) D



19. Assertion : p-nitrophenol is more viscous than o-nitrophenol.
Reason : In p-nitrophenol, intermolecular H-bonding occurs.
(1) A (2) B (3) C (4) D

20. Assertion : H_2O_2 is not used as solvent for ionic compounds
Reason : Dielectric constant of H_2O_2 is low
(1) A (2) B (3) C (4) D

21. Assertion : Ionic compounds exhibits electrical conductivity in solution state.
Reason : In solution state electrons of ionic compounds are free.
(1) A (2) B (3) C (4) D

22. Assertion : p-nitrophenol is more volatile than o-nitrophenol.
Reason : Molecular wt. of p-nitrophenol is higher than o-nitrophenol.
(1) A (2) B (3) C (4) D

23. Assertion : N_2^+ is more stable than N_2^-
Reason : N_2^+ has less electrons in antibonding orbitals.
(1) A (2) B (3) C (4) D

24. Assertion : SO_4^{2-} is square planar in shape
Reason : SO_4^{2-} has sp^3d hybridisation
(1) A (2) B (3) C (4) D

25. Assertion : NF_3 molecule is more polar than NH_3 molecule.
Reason : NF_3 is pyramidal while NH_3 is trigonal planar.
(1) A (2) B (3) C (4) D

26. Assertion : OF_4 does not exists.
Reason : Empty d-orbitals are absent in valence shell of oxygen.
(1) A (2) B (3) C (4) D

27. Assertion : BeCl_2 shows covalent character.
Reason : More polarization of Cl^- by Be^{+2} .
(1) A (2) B (3) C (4) D

28. Assertion : MgO and NaF are isomorphous
Reason : Crystal structure of MgO and NaF is identical.
(1) A (2) B (3) C (4) D

29. Assertion : NF_3 molecule is polar.
Reason : N-F bonds are polar.
(1) A (2) B (3) C (4) D

30. Assertion : NaCl is soluble in non polar solvents.
Reason : NaCl is a non-polar covalent compound.
(1) A (2) B (3) C (4) D

31. Assertion : Sigma bonds are stronger than π bonds.
Reason : Sigma bonds are covalent bonds.
(1) A (2) B (3) C (4) D

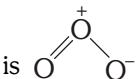
32. Assertion : CO_2 is non polar while SO_2 is polar molecule.
Reason : S-O bonds are polar while C-O non polar.
(1) A (2) B (3) C (4) D

33. Assertion : Both H_2O and SnCl_2 are bent molecules.
Reason : Both H_2O and SnCl_2 are sp^2 hybridised.
(1) A (2) B (3) C (4) D

34. Assertion : NO is paramagnetic in nature.
Reason : Bond order of NO is 2.5.
(1) A (2) B (3) C (4) D

35. Assertion : Nitrogen is unreactive at room temperature but becomes reactive at elevated temperature (on heating or in the presence of catalysts).
Reason : In nitrogen molecule, there is extensive delocalization of electrons.
(1) A (2) B (3) C (4) D

36. Assertion : NO_3^- is planar.
Reason : N in NO_3^- is sp^2 and no lone pair at central atom.
(1) A (2) B (3) C (4) D

37. Assertion : The electronic structure of O_3 is 
Reason :  Structure is not allowed because octet around 'O' can not be expanded.
(1) A (2) B (3) C (4) D

38. Assertion : LiCl is predominantly a covalent compound.
Reason : Electronegativity difference between 'Li' and 'Cl' is too small.
(1) A (2) B (3) C (4) D



39. **Assertion :-** Ozone is a powerful oxidizing agent in comparison to O_2 .
Reason :- Ozone is diamagnetic but O_2 is paramagnetic.
(1) A (2) B (3) C (4) D

40. **Assertion :-** B_2 molecule is diamagnetic.
Reason :- The highest occupied molecular orbital is of σ type.
(1) A (2) B (3) C (4) D

41. **Assertion :-** BH_4^- is known while BH_6^{-3} is not.
Reason :- B has very small atomic size.
(1) A (2) B (3) C (4) D

42. **Assertion :-** Some molecules are polar.
Reason :- The centre of negative charge and positive charge do not coincide each other in some molecule.
(1) A (2) B (3) C (4) D

43. **Assertion :-** $R_3P = O$ exists but $R_3N = O$ does not exists
Reason :- P is more electronegative than N
(1) A (2) B (3) C (4) D

44. **Assertion :-** ClF_3 has T-shape structure.
Reason :- It has two lone pair arrange at 180° (Angle).
(1) A (2) B (3) C (4) D

45. **Assertion :-** Bond Dissociation energy is $F_2 > Cl_2$.
Reason :- Cl_2 have more electronic repulsion than F_2 .
(1) A (2) B (3) C (4) D

46. **Assertion :-** H_2O molecule can form four hydrogen bonds.
Reason :- Two lone pairs and two hydrogens are directly attached with oxygen atoms.
(1) A (2) B (3) C (4) D

47. **Assertion :-** Bond angle in  is more than expected.
Reason :- It is due to lp-lp repulsion.
(1) A (2) B (3) C (4) D

EXERCISE-II (Assertion & Reason)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	4	2	2	3	2	3	3	3	3	3	3	3	1	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	2	4	3	1	3	3	4	1	4	4	1	1	1	2	4
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	2	3	3	2	3	1	1	3	2	4	2	1	3	3	4
Que.	46	47													
Ans.	1	3													

